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16. ABSTRACT

The document evaluates and assesses scientific information on the health and welfare effects associated with exposure to various concentrations of sulfur oxides and particulate matter in ambient air. The literature through 1980-81 has been reviewed thoroughly for information relevant to air quality criteria, although the document is not intended as a complete and detailed review of all literature pertaining to sulfur oxides and particulate matter. An attempt has been made to identify the major discrepancies in our current knowledge and understanding of the effects of these pollutants.

Although this document is principally concerned with the health and welfare effects of sulfur oxides and particulate matter, other scientific data are presented and evaluated in order to provide a better understanding of these pollutants in the environment To this end, the document includes chapters that discuss the chemistry and physics of the pollutants; analytical techniques; sources; and types of emissions; environmental concentrations and exposure levels; atmospheric chemistry and dispersion modeling; acidic deposition; effects on vegetation; effects on visibility, climate, and materials; and respiratory, physiological, toxicological, clinical, and epidemiological aspects of human exposure.

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Preface

This document is Volume II of a three-volume revision of *Air Quality Criteria for Particulate Matter* and *Air Quality Criteria for Sulfur Oxides*, first published in 1969 and 1970, respectively. By law, air quality criteria documents are the basis for establishment of the National Ambient Air Quality Standards (NAAQS). The Air Quality Criteria document of which this volume is a part has been prepared in response to specific requirements of Section 108 of the Clean Air Act, as amended in 1977. The Clean Air Act requires that the Administrator periodically review, and as appropriate, update and reissue criteria for NAAQS.

As the legally prescribed basis for deciding on National Ambient Air Quality Standards, the present document, *Air Quality Criteria for Particulate Matter and Sulfur Oxides*, focuses on characterization of health and welfare effects associated with exposure to particulate matter and sulfur oxides and pollutant concentrations which cause such effects. The major health and welfare effects of particulate matter and sulfur oxides are discussed in Chapters 8 through 14 in Volume III of this document. To assist the reader in putting the effects into perspective with the real-world environment, Chapters 2 through 7 in the present volume (Volume II) have been prepared. The chapters of Volume II discuss essential points regarding: physical and chemical properties; air monitoring and analytical measurement techniques; sources and emissions; transport, transformation, and fate; and observed ambient concentrations of the pollutants. Also, Chapter 7 in this volume introduces the reader to the contemporary problem of acidic deposition and potential contributions of sulfur oxides to acidic deposition phenomena.

Volume I introduces the criteria document, explains the rationale behind combining the evaluation of criteria for particulate matter and sulfur oxides in a single document and briefly summarizes the content of the entire criteria document. However, for a fuller understanding of the health and welfare effects of particulate matter and sulfur oxides, both Volumes II and III of the document should be consulted.

The Agency is pleased to acknowledge the efforts of all persons and groups who have contributed to the preparation of this document. In the last analysis, however, the Environmental Protection Agency accepts full responsibility for its content.

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2. PHYSICS AND CHEMISTRY OF SULFUR OXIDES AND PARTICULATE MATTER

2.1 INTRODUCTION

This chapter presents the current state of knowledge of the chemistry and physics of sulfur oxides (SO_x) and particulate matter (PM) that is pertinent to tropospheric phenomena, effects, and sampling methodology. The 1970 Air Quality Criteria for Sulfur Oxides (National Air Pollution Control Administration, 1970) and the 1969 Air Quality Criteria for Particulate Matter (National Air Pollution Control Administration, 1969) at the time of their publication adequately described the existing knowledge of the ambient chemistry and physics of sulfur oxides and particulate matter. However, significant progress has been made since that time in understanding tropospheric properties and processes. While this chapter focuses mainly on advances made in the past decade, earlier work is mentioned for the sake of comprehensiveness.

This chapter is organized into three principal parts, as follows:

A. Atmospheric domain and processes
  --global sulfur cycle
  --atmospheric sulfur cycle
  --pathways and processes

B. Physics and chemistry of sulfur oxides
  --gaseous physical properties
  --solution physical properties
  --gas-phase chemical reactions (elementary rate consists for SO_2 oxidation; influence of volatile organics and nitrogen oxides)
  --solution-phase chemical reactions (reactions kinetics for oxidation by O_3, H_2O_2, and catalysts; limitations of reported studies)
  --surface chemical reactions (metal oxides and carbon)

C. Physics and chemistry of particulate matter
  --definitions of aerosol science terms
  --physical properties of gases and particles (size, shape, density, morphology, charging, adhesion, vapor pressure; optics are discussed in Chapter 9)
  --dynamics of single particles (sedimentation, impaction, diffusion, electrodynamics)
  --formation and growth of particles (nucleation, coagulation, condensation, gas-particle chemical reaction)
  --characterization of atmospheric aerosol (size, distribution by number, area, volume, and mass distributions; composition of fine and coarse particle mass fractions)

Available evidence leads to the following conclusions:

A. The physics and chemistry of SO_2

1. The thermodynamic properties, molecular structure and bonding, and electromagnetic absorption spectra in air and dissolved in water are well established, except for hygroscopic/deliquescent properties of internally mixed salts.

2. Of the homogeneous gas-phase SO_2 oxidation reactions, only three have been identified as likely being significant in the troposphere:

   a. HO radical attack on SO_2
   b. HO_2 radical attack on SO_2
   c. CH_3O_2 radical attack on SO_2

3. The auto-oxidation (uncatalyzed) reaction of SO_2 dissolved in liquid water is too slow to be an important reaction in the troposphere.

4. The Mn(II)- and Fe(III)-catalyzed oxidation of SO_2 dissolved in liquid water may be an important reaction in the troposphere. However, there is serious doubt regarding the rate expression for th Mn(II)-catalyzed oxidation.

5. The effectiveness of Cu(II), V(V), V(IV), Ni(II), Zn(II), and Pb(II) as catalysts for the oxidation of SO_2 dissolved in liquid water are unknown.

6. Lack of data on the effectiveness of dissolved organics and of bicarbonate ion (HCO_3^-) as inhibitors prevents the confident use of aqueous-phase SO_2 catalyzed oxidation rate expressions for tropospheric model prediction.

7. Elemental carbon (soot) particles coated with an aqueous film may be important catalysts for SO_2 oxidation in the troposphere.

8. The reaction rate expressions of dissolved O_3 and dissolved NO_2 with dissolved SO_2 species are known, but these reactions appear to be ineffective for sulfate formation in the troposphere.

9. The rate expression for dissolved H_2O_2 and dissolved SO_2 species is known and appears to be a highly effective reaction for sulfate formation in the troposphere.

10. SO_2 reactions with solid-particle surfaces are not effective for sustained SO_4^{2-} formation in the troposphere.

B. The physics and chemistry of particulate matter

1. The physical properties of gases that affect aerosol behavior are well known.

2. The physical characteristics of tropospheric particles are highly variable, but the physics through which they influence aerosol behavior is well known.

3. The particle mass distribution function ($\Delta M/\Delta$ log Diam. v. log Diam.) for tropospheric aerosols over land is often multimodal. The fine particles (diameter less than about 2 μm) may have two (or more) modes, usually at about 0.02 μm and at about 0.2 μm. The coarse particles (greater than 2.5 μm) generally have one mode in the range 5 to 50 μm.

4. The mass composition of the coarse particles is dominated by minerals whose direct source types are well-known.

5. The mass composition of the fine particles is dominated by SO_4^{2-}, organics, elemental carbon (soot), NO_3^- and NH_4^+ whose direct and indirect source types are quantitatively well known.

6. The detailed chemical pathways for forming the SO_4^{2-}, organics, and NO_3^- found in the fine particles have not been established.

7. Strong acids are often found in the fine mass fraction, while bases are found in the coarse mass fraction.

8. The molecular composition of the organic components (generally found in the fine mass fraction) is not well characterized.

9. Water is the major constituent of the particle mass, but the deliquescence and hygroscopic properties of mixed salts cannot be predicted reliably.

10. The dynamics of motion of a particle with a diameter of less than 10 μm can best be described in terms of the physical characteristics of the particle, the force fields present, and the motion of the suspending gas. However, this ability does not adequately extend to larger particles, especially in the presence of nonsteady force fields and motions of the suspending gas. This limitation requires empirical design of inlets or the use of non-aspirating methods for particles with diameters greater than about 10 μm.

11. Fundamental questions remain about the aerosol processes of nucleation, condensation, and coagulation, but these processes are understood sufficiently to explain and predict the qualitative behavior of aerosols in the troposphere.

12. Atmospheric observations confirm theoretical predictions that condensation, gas-particle reactions, and coagulation are important processes only for the growth of fine particles as opposed to coarse particles.

2.2 ATMOSPHERIC DOMAIN AND PROCESSES

Scientists are interested in the physical properties and chemistry of SO_x and PM because sulfur has an important natural cycle (see Figure 2-1) in the environment. It undergoes various oxidation and reduction reactions and translocations among the atmosphere, biosphere, hydrosphere, pedosphere, and lithosphere. Human activity (especially fossil-fuel combustion) has added a major perturbation to the natural cycle, and possibly modified natural rates and reservoirs. The fluxes of sulfur translocation between reservoirs have been estimated for the paths numbered in Figure 2-1. Several estimates of annual fluxes are presented in Table 2-1. The agreement among the reported values is not good; for example, the estimates of annual anthropogenic sulfur fluxes to the atmosphere range from 11 to 45 percent of the total sulfur involved in the atmospheric balance. The global cycles of carbon and nitrogen and their mutual inter-actions with the sulfur cycle are important, but are too complex to present here.

While the global sulfur cycle (Figure 2-1) and the annual fluxes of sulfur between compartments (Table 2-1) provide a broad view of the processes that may lead to adverse impacts upon mankind and ecological systems, the global scale is clearly beyond the scope of this

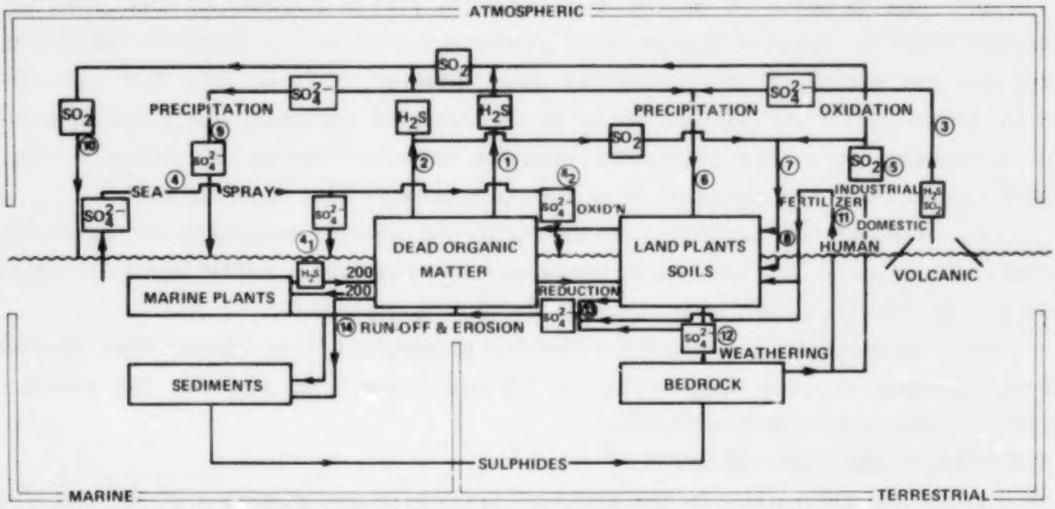
ATMOSPHERIC
SO_2
SO_4^{2-}
SO_4^{2-}
SO_2
⑩
PRECIPITATION
⑨
SO_4^{2-}
H_2S
H_2S
②
①
SO_2
PRECIPITATION
OXIDATION
③
⑦
SO_2
⑤
⑥
8_2
SEA
④
SPRAY
SO_4^{2-}
SO_4^{2-}
SO_4^{2-}
OXID'N
INDUSTRIAL
FERTILIZER
⑪
DOMESTIC
HUMAN
H_2S
SO_2
4_1
H_2S
200
200
DEAD ORGANIC MATTER
LAND PLANTS SOILS
⑧
VOLCANIC
MARINE PLANTS
REDUCTION
SO_4^{2-}
⑬
⑭ RUN-OFF & EROSION
SO_4^{2-}
⑫
WEATHERING
SEDIMENTS
BEDROCK
SULPHIDES
MARINE
TERRESTRIAL

Figure 2-1. The global sulfur cycle, showing the major reservoirs, pathways, and forms of occurrence of sulfur. Figures enclosed in circles (e.g., 1) refer to the individual fluxes and correspond to figures in column 1, Table 2-1.

Source: Moss (1978).

TABLE 2-1. ESTIMATES[a] OF ENVIRONMENTAL SULFUR ANNUAL FLUXES (TG/YEAR)

Source of sulfur	Flux number in Figure 2-1	Eriksson (1960,1963)	Robinson and Robbins (1968,1970)	Kellogg et al., (1972)	Friend (1973)	Granat et al. (1976)
Biological decay (land)	1	110	68		58	5
Biological decay (ocean)	2	170	30	90	48	27
Volcanic activity	3	--	--	1.5	2	3
Sea spray (total)	4	45	44	47	44	44
To ocean	4_1	(40)	--	(43)	(40)	(40)
To land	4_2	(5)	--	(4)	(4)	(4)
Anthropogenic	5	40	70	50	65	65
Precipitation (land)	6	65	70	86	86	43
Dry deposition	7	100	20	10	20	28
Absorption (vegetation)	8	75	26	15	15	
Precipitation and dry deposition (ocean)	9	100	71	72	71	73
Absorption (ocean)	10	100	25	--	25	
Total sulfur involved in atmospheric balance		365	212	183	217	144
Atmospheric balance						
Land → sea		-10	+26	+5	+8	+18
Sea → land		5	4	4	4	17
Fertilizer	11	10	11	--	26	--
Rock weathering	12	15	14	--	42	--
Pedosphere → river runoff	13	55	48	--	89	--
Total river runoff	14	80	73	--	136	122

Note: The numbers in parentheses for sub-pathways 4_1 and 4_2 are estimates of the decomposition of the total pathway 4.

[a] Sources: As cited in each column and, in part, Friend (1973, Table 4).

document. Also, the sulfur and particulate matter emissions are not uniformly distributed over the land mass of the United States, nor is the time scale of one year adequately sensitive to relate emissions to effects.

Cause-effect relationships are described in terms of length and time scales. Consequently, any discussion of the atmospheric physics and chemistry of sulfur oxides and particulate matter must be in terms of those length and time scales. The characteristic time and length scales for typical effects are shown in Table 2-2; also given are the parameters that control the functions relating the effects to pollutants. The relationships of emissions to effects, as shown in Table 2-2, require that we understand the physics and chemistry of sulfur oxides and particulate matter on time scales of one hour to decades and length scales of 1 cm to thousands of kilometers. With these constraints, our attention is focused on that portion of the global sulfur cycle that consists of the perturbed atmosphere over land surfaces. Most of the natural and anthropogenic emissions of sulfur and PM are contained within the troposphere, which is the layer of air contained in the zone from ground level to a height of 12 ± 5 km. This zone contains most of the pollutants emitted into the atmosphere.

Thus, in order to understand the relationships between sources and effects, it is necessary to have detailed knowledge of the pathways, properties, and processes that are shown in Figure 2-2.

TABLE 2-2. CHARACTERISTIC TIMES AND LENGTHS FOR OBSERVATION OF EFFECTS

Types of Effects	Function	Time	Length
Damage to ecosystems and materials due to SO_2 and particulate mass deposition (see Chapters 7, 8 and 10)	Acid flux (= acid and SO_2 mass concentration x deposition velocity)	Hours to years	$10\text{-}10^3$ km
Loss of visual quality (see Chapter 9)	Mass concentration, particle size distribution, and composition	Hours to days	$10\text{-}10^3$ km
Climate modification (see Chapter 9)	Atmospheric burden of particle mass, particle size, and composition	Decades	Global
Damage to human lungs due to SO_2 and particulate inhalation/deposition (see Chapters 11 & 12)	Mass concentration, particle size distribution, composition	Hours to years	< 1 cm

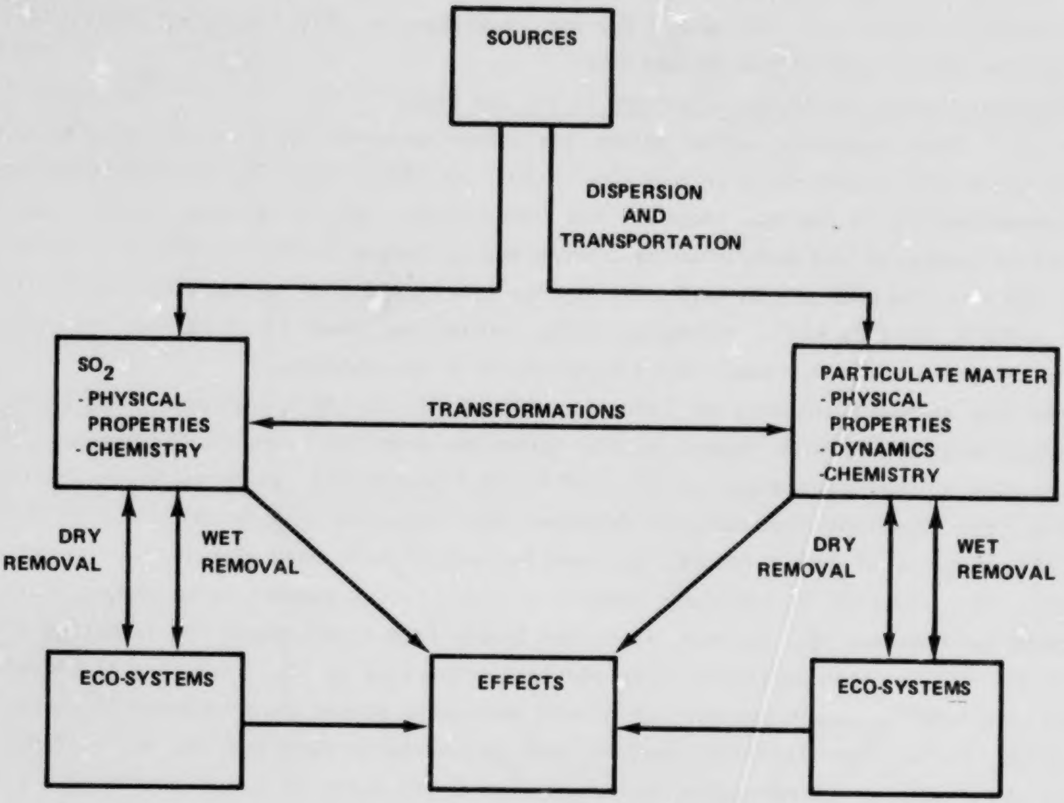
SOURCES
DISPERSION AND TRANSPORTATION
SO_2
- PHYSICAL PROPERTIES
- CHEMISTRY
TRANSFORMATIONS
PARTICULATE MATTER
- PHYSICAL PROPERTIES
- DYNAMICS
-CHEMISTRY
DRY REMOVAL
WET REMOVAL
DRY REMOVAL
WET REMOVAL
ECO-SYSTEMS
EFFECTS
ECO-SYSTEMS

Figure 2-2. Inter-relations of pathways, processes, and properties of sulfur oxides and particulate matter and effects.

This chapter discusses the state of knowledge of physical properties, chemistry, and gas-to-aerosol transformations. The dry and wet removal pathways are discussed in Chapter 6, which also addresses modeling of atmospheric dispersion, transport, transformation, and removal.

2.3 PHYSICS AND CHEMISTRY OF SULFUR OXIDES

Knowledge of the physics and chemistry of sulfur oxides is necessary for designing satisfactory samplers and monitors, understanding relationships between sources and effects, and understanding important tropospheric processes, e.g., chemical transformations and deposition.

In Section 2.3, the physical properties and reaction chemistry of sulfur oxides in the gas and solution phases are reviewed. Current knowledge in these important areas is summarized at the end of each of the subsections.

2.3.1 Physical Properties of Sulfur Oxides in the Gas Phase

The four known monomeric sulfur oxides are sulfur monoxide (SO), sulfur dioxide (SO_2), sulfur trioxide (SO_3), and disulfur monoxide (S_2O). Of these, only SO_2 is present at significant concentrations in the gas phase of the troposphere. SO_3 is emitted directly into the atmosphere by combustion and manufacturing sources and is formed in the atmosphere by oxidation of SO_2. However, because of its high affinity for water (H_2O), it reacts within milliseconds to form sulfuric acid (H_2SO_4). Polymeric sulfur oxides are known to exist, but they are not stable in the presence of H_2O vapor and are not found in the atmosphere.

Since the standard enthalpy of formation $\Delta H°$ of SO_2 is -70.9 kcal/mole (25°C), SO_2 is thermodynamically stable with regard to its formation from the elements (Glasstone, 1947). SO_2 is capable of being oxidized to SO_3 ($\Delta H° = -94.4$ kcal/mole), which yields H_2SO_4 in the atmosphere (the important tropospheric reactions are discussed in Sections 2.3.3 to 2.3.5). SO_2 is also capable of being reduced by reaction with H_2S to form elemental S (the Clauss Reaction). This reaction is important commercially but is not thought to be important in the troposphere for removing SO_2; however, it is the likely formation pathway for formation of the elemental S found in urban particles. The physical properties of SO_2, including its molecular structure and bonding, vapor pressure of liquid and solid phases, electromagnetic absorption (ultraviolet, visible, and infrared) spectra, and thermodynamic constants are well established. Extensive descriptions and references to original work are given by Schenk and Steudel (1968) and Schroeter (1966).

The physical properties of gaseous SO_2 are well known.

2.3.2 Solution Physical Properties

Knowledge of the physical properties of dissolved SO_2 solution species and sulfates is required for sampler design, interpretation of laboratory measurements of SO_2 oxidation, and modeling SO_2 oxidation in particles, fog, and rain.

2.3.2.1 Sulfur Dioxide--SO_2 dissolves in H_2O to form these species: $SO_2 \cdot H_2O$, HSO_3^-, and SO_3^{2-}. Although the formation of sulfurous acid, H_2SO_3, is often postulated instead of $SO_2 \cdot H_2O$, it has not been observed (Lyons and Nickless, 1968). The electronic absorption spectra (Hayon et al., 1972), redox potentials (Valensi et al., 1966), and structure and bonding (Lyons and Nickless, 1968) of HSO_3^- and SO_3^{2-} are known. The formation of these species in water occurs through the equilibrium reactions given in Table 2-3. Eigen et al. (1961) measured the forward (k_{+1}) and reverse (k_{-1}) rate constants at 20°C for reaction:

$$SO_2 \cdot H_2O \rightleftarrows H^+ + HSO_3^- \qquad (2\text{-}1)$$

and found that

$$k_{+1} = 3.4 \times 10^6 s^{-1}$$

$$k_{-1} = 2 \times 10^8 M^{-1} s^{-1},$$

which are in good agreement with the thermodynamic value of K_{A1} in Table 2-3. These measurements are important because they demonstrate that the $SO_2 \cdot H_2O$ - HSO_3^- reaction will achieve equilibrium within 1 μs of a perturbation. The rate constants k_{+2} and k_{-2} for the reaction

$$HSO_3^- \leftrightarrows H^+ + SO_3^{2-} \qquad (2\text{-}2)$$

are unknown. It is reasonable that the value of the protonation rate constant (k_{-2}) is less than the theoretical diffusion limit ($\sim 5 \times 10^{10} M^{-1} s^{-1}$), but greater than k_{-1}. The expected range of k_{+2} is therefore $(0.008\text{-}2) \times 10^3 s^{-1}$, which means that SO_3^{2-} will achieve equilibrium concentration within 0.5-125 ms of a perturbation. Thus, the equilibrium distribution of $SO_2 \cdot H_2O$, HSO_3^-, and SO_3^{2-} is expected to be achieved with a relaxation time of 0.5 to 125 ms. This time is too short to impact SO_4^{2-} formation rates in particles, mists, and rain; that is, equilibrium conditions can be assumed to be continuously satisfied in these liquid systems. However, the relaxation times need to be considered in interpreting the kinetics of rapid oxidation, such as measured in flash photolysis and flash radiolysis experiments.

An important feature of the $SO_2 \cdot H_2O$ - HSO_3^- - SO_3^{2-} system is the influence of H^+ in governing the distribution of these species and the ratio of $SO_{2(g)}$ to total dissolved S(IV) species concentrations, as shown in Figure 2-3. The oxidation rate of this system is often pH dependent, indicating different oxidation rates for the three species. The oxidation reactions are discussed in Section 2.3.4.

Sulfite ion forms stable complexes with many metal ions, especially those in Periodic Group VIII (Lyons and Nickless, 1968). The possible formation and significance of stable transition metal ion-sulfite complexes have been suggested (Eatough et al., 1978; Hilton et al., 1979), but contrary evidence has been reported (Dasgupta et al., 1979). At this time, the issue is unresolved (Eatough et al., 1979). The formation of the stable complex dichlorosulfonatomercurate ion is the basis of the West-Gaeke method for determining SO_2 in the air (see Chapter 3).

The physical properties of dissolved SO_2 and its water-association products are well known.

TABLE 2-3. DILUTE SULFUR DIOXIDE-WATER SYSTEM

Reaction	Constant (25°C)
$SO_{2(g)} + H_2O_{(\ell)} \rightleftarrows SO_2\cdot H_2O$	$\underline{H} = 0.0332$
$SO_2\cdot H_2O \rightleftarrows H^+ + HSO_3^-$	$K_{A1} = 1.39 \times 10^{-2}$ $pK_{A1} = 1.86$
$HSO_3^- \rightleftarrows H^+ + SO_3^{2-}$	$K_{A2} = 4 \times 10^{-8}$ $pK_{A2} = 7.40$

Notes:

1. $\underline{H}$ = Henry's law constant (dimensionless)

   = ($SO_{2(g)}$ molar concentration)/($SO_2\cdot H_2O$ molar concentration)

   Source of value: Hales and Sutter (1973)

2. K_{A1} = dissociation constant, mole/liter

   $= (a_{H^+})(a_{HSO_3^-})/(a_{SO_2\cdot H_2O})$

   $\simeq [H^+][HSO_3^-]/[SO_2\cdot H_2O]$ (for dilute solutions)

   where

   a_i = activity of species i, mole/liter

   $[i]$ = concentration of species i, mole/liter

   Source of value: Huss and Eckert (1977)

3. K_{A2} = dissociation constant, mole/liter

   $= (a_{H^+})(a_{SO_3^{2-}})/(a_{HSO_3^-})$

   $\simeq [H^+][SO_3^{2-}]/[HSO_3^-]$ (for dilute solutions)

   Source of value: Salomaa et al. (1969)

4. The ratio of dilute concentrations of $SO_{2(g)}$ to the total quantity dissolved in water is given by:

$$\frac{[SO_{2(g)}]}{[S(IV)]} = \frac{[SO_{2(g)}]}{[SO_2\cdot H_2O] + [HSO_3^-] + [SO_3^{2-}]}$$

$$= \underline{H}(1 + K_{A1}[H^+]^{-1} + K_{A1}K_{A2}[H^+]^{-2})^{-1} .$$

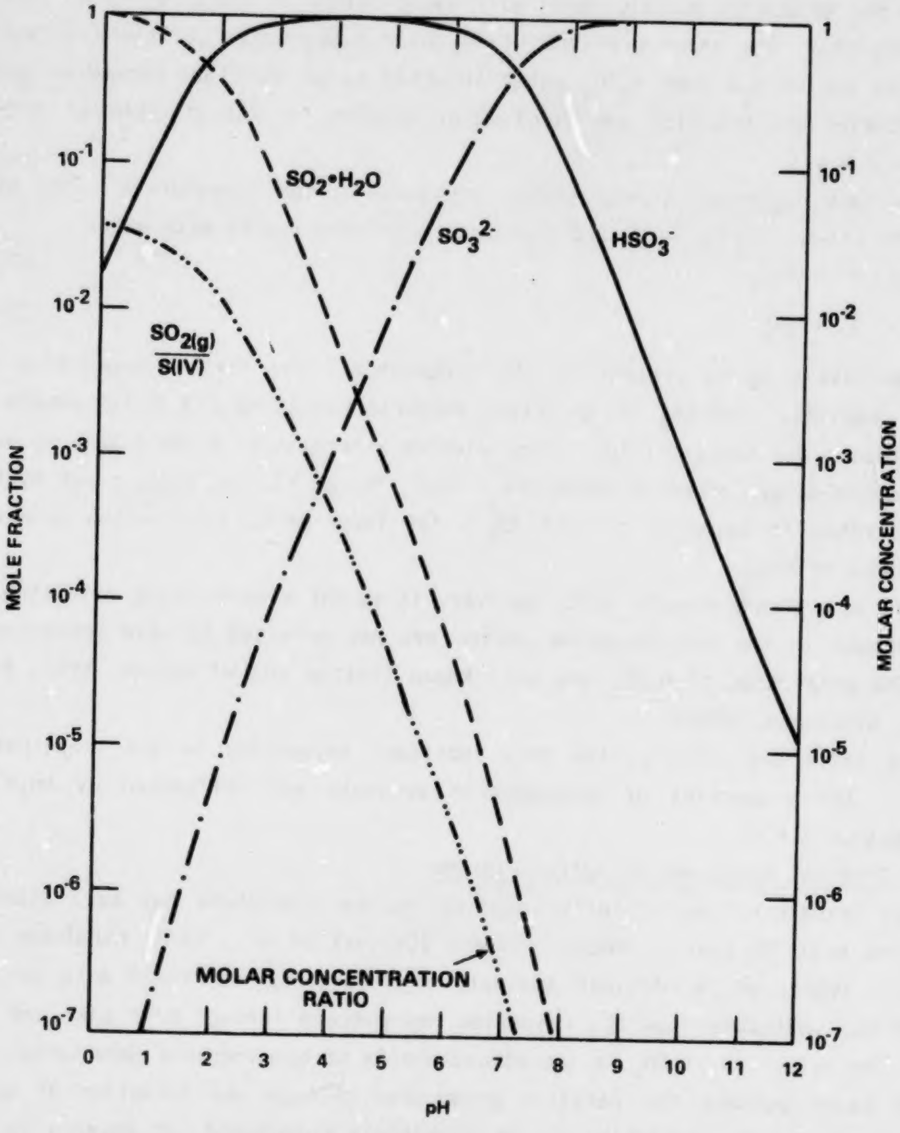

Figure 2-3. The distribution of species for the $SO_2 \cdot H_2O$—HSO_3^-—SO_3^{2-} system as a function of pH. Also, the ratio of the concentrations of $SO_{2(g)}$ to the total quantity dissolved in water is shown; see Table 2-3, Note 4.

2.3.2.2 Sulfur Trioxide and Sulfuric Acid--Knowledge of the properties of SO_3 and H_2SO_4 are important for the design of samplers and monitors, and for understanding the behavior of ambient particles, fogs, and rain.

SO_3 has a high affinity for water and is not present at significant concentrations in the atmosphere. Free SO_3 molecules quickly react with water molecules and droplets to form H_2SO_4 water solution droplets. The vapor pressure of SO_3 over H_2SO_4 water solutions is extremely low; the vapor pressure of H_2O over H_2SO_4 water solution is an important parameter governing nucleation of particles and the size and pH of water droplets in the atmosphere. (See discussion in Section 2.4.4.)

H_2SO_4 is the only important strong sulfur oxy acid in the troposphere. Its solution properties are well known. H_2SO_4 is a strong dibasic acid that reacts with water:

$$H_2SO_4 \rightarrow H^+ + HSO_4^- \qquad (2\text{-}3)$$

$$HSO_4^- \rightarrow H^+ + SO_4^{2-} \qquad (2\text{-}4)$$

For water systems likely to be present in the troposphere, the first dissociation can be considered to be complete. The pK_A of the first dissociation is -3 and of the second dissociation is ~2 (Robinson and Stokes, 1970). The relative strengths of acids likely to be found in tropospheric particles are shown in Table 2-4. Thus, for pH >3, the H_2SO_4 - H_2O system can adequately be described in terms of H^+ and SO_4^{2-}; for lower pH's, it is often necessary to consider the presence of HSO_4^-.

Sulfuric acid is a strong dibasic acid; however, it is not a very strong oxidizing agent. Metals below hydrogen in the electromotive series are not oxidized by cold concentrated or dilute H_2SO_4. The properties of H_2SO_4 are well known (Cotton and Wilkerson, 1967; Robinson and Stokes, 1970; Gillespie, 1968).

Most sulfate salts are soluble; the only important exceptions in the troposphere are $CaSO_4$ and $PbSO_4$. The properties of tropospheric aerosols are influenced by NH_4HSO_4 and $(NH_4)_2SO_4$ (see Section 2.4.4).

2.3.3 Gas-Phase Chemical Reactions of Sulfur Dioxide

The chemical transformation of sulfur dioxide in the atmosphere has been studied extensively over the past 20 years. Recent reviews (Calvert et al., 1978; Middleton et al., 1980; and Möller, 1980), which consider analysis of laboratory and field data as well as theoretical studies, indicated that SO_2 oxidation may proceed through both gas- and liquid-phase ractions. The oxidation of SO_2 in the atmosphere is of considerable importance, in that it represents a major pathway for particle production through the formation of sulfates. Although the mechanism of SO_2 oxidation is not completely understood, it appears to proceed via four pathways: homogeneous gas phase reactions; heterogeneous gas-solid interface reactions; and catalyzed and uncatalyzed liquid phase reactions. Homogeneous gas phase reactions are by far the most extensively studied and best understood quantitatively.

TABLE 2-4. RELATIVE STRENGTHS OF ACIDS IN WATER SOLUTION (25°C)

Acid Dissociation	pK_A (= -Log K_A)	Reference
$HI \rightleftarrows H^+ + I^-$	-10	Cotton & Wilkerson (1980)
$HBr \rightleftarrows H^+ + Br^-$	-9.5	Cotton & Wilkerson (1980)
$HCL \rightleftarrows H^+ + CL^-$	-7	Cotton & Wilkerson (1980)
$H_2SO_4 \rightleftarrows H^+ + HSO_4^-$	-3	Robinson & Stokes (1970)
$HNO_3 \rightleftarrows H^+ + NO_3^-$	-1.3	Robinson & Stokes (1970)
$H_2O \cdot SO_2 \rightleftarrows H^+ + HSO_3^-$	1.86	Huss & Eckert (1977)
$HSO_4^- \rightleftarrows H^+ + SO_4^{2-}$	1.92	Cotton & Wilkerson (1980)
$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$	2.12	Cotton & Wilkerson (1980)
$HF \rightleftarrows H^+ + F^-$	3.2	Cotton & Wilkerson (1980)
$HNO_2 \rightleftarrows H^+ + NO_2^-$	3.3	Cotton & Wilkerson (1980)
$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$	6.38	Cotton & Wilkerson (1980)
$H_2S \rightleftarrows H^+ + HS^-$	7.0	Cotton & Wilkerson (1980)
$HSO_3^- \rightleftarrows H^+ + SO_3^{2-}$	7.4	Salomaa et al. (1969)
$HCN \rightleftarrows H^+ + CN^-$	9.21	Cotton & Wilkerson (1980)
$NH_4^+ \rightleftarrows H^+ + NH_3$	9.25	Cotton & Wilkerson (1980)
$HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$	10.3	Cotton & Wilkerson (1980)
$H_2O \rightleftarrows H^+ + OH^-$	14.0	Cotton & Wilkerson (1980)

The homogeneous gas-phase chemistry of oxidation in the clean and the polluted troposphere is reviewed in this section. The current status of knowledge is presented for the elementary oxidation reactions of SO_2 and the importance of volatile organic and nitrogen oxides as generators of free radical oxidizers. This review will show that the photochemical oxidation of SO_2 may be a significant pathway for tropospheric sulfate formation. The three most important oxidizers of SO_2 are: hydroxyl radical, HO; peroxyl radical, HO_2; and methylperoxyl radical, CH_3O_2. At this time, only the reaction rate constant for HO is well established. The pathways of formation of the oxidizer radicals for the unpolluted troposphere can be explained in terms of the photochemistry of the $NO-CH_4-CO-O_3$ system. In polluted atmospheres, volatile organics and oxides of nitrogen act together to produce additional radicals and accelerate overall radical production. There is also evidence that a dark reaction among O_3, alkenes, and SO_2 is effective in oxidizing SO_2.

2.3.3.1 Elementary Reactions--The elementary chemical reactions of SO_2 in air have been the subject of intense investigation. Studies prior to 1965 have been critically reviewed by Altshuller and Bufalini (1971), and more recently by Calvert et al. (1978). Calvert et al. (1978) systematically examined the rate constants and significance of SO_2 elementary reactions known to occur in the troposphere. Identified as generally unimportant reactions were: photodissociation; photoexcitation; reaction with singlet delta oxygen, $O_2('\Delta_g)$; reaction with atomic oxygen, $O(^3P)$; reaction with ozone, O_3; reaction with nitrogen oxides (NO_2, NO_3, N_2O_5); reaction with tert-butylperoxyl radical, $(CH_3)_3CO_2$; and reaction with acetylperoxyl radical, CH_3COO_2. The only SO_2 reactions in the troposphere that were identified as important were those due to HO, HO_2, and CH_3O_2. The rate constants recommended by Calvert et al. (1978) for these three reactions are given in Table 2-5. More recent work is in conflict with the rate constants for HO_2 and CH_3O_2 that have been recommended by Calvert et al. (1978). Graham et al. (1979) and Burrows et al. (1979) have reported rate constants for the HO_2 reaction that are much lower than that recommended by Calvert et al. (1978). Also, Sander and Watson (1981) have reported a rate constant for the CH_3O_2 reaction that is much lower than that recommended by Calvert et al. (1978). These more recent values are given in Table 2-5. The reasons for the discrepancies in these two rate constants are unknown, and there is no basis to recommend preferred values.

Although the dark reaction of $SO_2 + O_3$ is too slow to be important in the troposphere, the addition of alkenes greatly enhances the oxidation rate. The experimental work of Cox and Penkett (1971a,b; 1972) and McNelis et al. (1975) has been reviewed and reevaluated by Calvert et al. (1978). The reaction system is too complex to discuss here, but Calvert et al. (1978) report results of their calculations for total alkenes = 0.10 ppm, $[O_3]$ = 0.15 ppm, and $[SO_2]$ = 0.05 ppm; they estimated that the disappearance rate of SO_2 is 0.23 and 0.12 percent/h at 50 and 100 percent relative humidity (25°C), respectively. The reaction mechanism for the O_3 +

TABLE 2-5. RATE CONSTANTS FOR HYDROXYL, PEROXYL, AND METHOXYL RADICALS

Reaction	Second order rate constant,[a] $cm^3 mole^{-1} s^{-1}$	Source
$HO + SO_2 \rightarrow HOSO_2 \rightarrow H_2SO_4$	$(1.1 \pm 0.3) \times 10^{-12}$	Calvert et al. (1978)
$HO_2 + SO_2 \rightarrow HO + SO_3 \rightarrow H_2SO_4$	$>(8.7 \pm 1.3) \times 10^{-16}$	Calvert et al. (1978)
	$<1 \times 10^{-18}$	Graham et al. (1979)
	$\leq 2 \times 10^{-17}$	Burrows et al. (1979)
$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3 \rightarrow H_2SO_4$	$(5.3 \pm 2.5) \times 10^{-15}$	Calvert et al. (1978)
	5×10^{-17}	Sander and Watson (1981)

[a] Temperature = 25°C.

alkene + SO_2 system is not known, but studies by Niki et al. (1977) and Su et al. (1980) indicate that the reactive species may be the biradical (RCHOO) formed by the decomposition of the original molozonide.

In summary:

1. Three gas-phase tropospheric oxidation reactions have been identified as being possibly important:
   a. HO radical. The rate constant appears to be well established.
   b. HO_2 radical. The rate constant is not well established.
   c. CH_3O_2 radical. The rate constant is not well established.
2. $SO_2 + O_3$ + alkenes may be an important dark reaction.

2.3.3.2 Tropospheric Chemistry of Sulfur Dioxide Oxidation--The chemistry of the clean troposphere and its mathematical simulation have been studied extensively by Levy (1971), Wofsy et al. (1972), Crutzen (1974), Fishman and Crutzen (1977), Chameides and Walker (1973, 1976) and Stewart et al. (1977).

The photochemistry of the unpolluted troposphere develops around a chain reaction sequence involving NO, CH_4, CO and O_3. The photochemical reaction chain sequence in the troposphere is initiated by HO formed from the interaction of $O(^1D)$, the product of photolysis of O_3 in the short wavelength portion of the solar spectrum, with H_2O.

$$O_3 + h\nu(\lambda \leq 310\ nm) \rightarrow O(^1D) + O_2 \qquad (2-5)$$

$$O(^1D) + H_2O \rightarrow 2HO \qquad (2-6)$$

The HO produced reacts with CH_4 and CO present in the clean troposphere, resulting in the generation of peroxyl radical species, HO_2, CH_3O_2.

$$HO + CH_4 \rightarrow CH_3 + H_2O \quad (2\text{-}7)$$

$$HO + CO \rightarrow H + CO_2 \quad (2\text{-}8)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad (2\text{-}9)$$

$$H + O_2 + M \rightarrow HO_2 + M \quad (2\text{-}10)$$

In turn, the peroxyl radicals participate in a chain propagating sequence which converts nitric oxide (NO) to nitrogen dioxide (NO_2) and in the process produces additional hydroxyl and peroxyl radical species.

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad (2\text{-}11)$$

$$HO_2 + NO \rightarrow HO + NO_2 \quad (2\text{-}12)$$

$$CH_3O + O_2 \rightarrow HO_2 + H_2CO \quad (2\text{-}13)$$

$$H_2CO + h\nu(\lambda \leq 370 \text{ nm}) \rightarrow H + HCO \quad (2\text{-}14)$$

$$HCO + O_2 \rightarrow HO_2 + CO \quad (2\text{-}15)$$

$$H_2O_2 + HO \rightarrow H_2O + HO_2 \quad (2\text{-}16)$$

The major chain terminating steps include:

$$HO + NO_2 + M \rightarrow HONO_2 + M \quad (2\text{-}17)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (2\text{-}18)$$

The reaction sequence for O_3 production involves converting NO to NO_2 at a rate sufficiently high to maintain a NO_2/NO ratio to sustain the observed background levels of O_3.

$$HO_2 + NO \rightarrow HO + NO_2 \quad (2\text{-}12)$$

$$NO_2 + h\nu \rightarrow NO + O \quad (2\text{-}19)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (2\text{-}20)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (2\text{-}21)$$

$$HO + CO \rightarrow H + CO_2 \quad (2\text{-}8)$$

In general, reactions (19) through (21) govern the O_3 concentration levels present in the sunlight irradiated well-mixed atmosphere at any instant and to a first approximation the steady state relationship, Leighton (1961),

$$\frac{(NO_2)\, k_{19}}{(NO)\, k_{21}} = (O_3)$$

provides an accurate estimate of O_3 given the ratio of $(NO_2)/(NO)$ and k_{19}/k_{21}. The photolytic rate constant k_{19} is directly related to the integrated actinic solar flux over the wavelength range 290 - 430 nm.

The paths for O_3 net destruction in the troposphere include the reaction sequence

$$HO_2 + O_3 \rightarrow HO + 2O_2 \qquad (2\text{-}22)$$

$$HO + O_3 \rightarrow HO_2 + O_2 \qquad (2\text{-}23)$$

Hydroxyl radical abundances predicted by the tropospheric photochemical models, 10^5 to 10^6 molec cm^{-3}, are in qualitative agreement with recent measurements by Davis et al. (1976), Perner et al. (1976), and Campbell et al. (1979) and inferred HO levels based on measured trace gas abundances in the troposphere by Singh (1977).

In the case of the chemistry of polluted atmospheres, extensive discussions on the mechanism of photochemical smog and its computer simulation have been presented by Demerjian et al. (1974), Calvert and McQuigg (1975), Niki et al. (1972), Hecht et al. (1974), and Carter et al. (1979).

Perturbations of the photochemical oxidation cycle within the atmosphere introduced by anthropogenic emissions are predominately caused by two classes of compounds, volatile organic compounds and nitrogen oxides. The reaction chain sequence discussed earlier for the clean troposphere has now been immensely complicated by the addition of scores of volatile organic compounds which participate in the chain propagating cycle. Figure 2-4 depicts a schematic of the polluted atmospheric photooxidation cycle. The addition of volatile organic compounds (VOC) in the atmosphere introduces a variety of new peroxyl radical species.

In its simplest form, the photochemical oxidation cycle in polluted atmospheres is governed by the following basic features. Free radical attack on atmospheric VOC's is initiated by a select group of compounds, which are for the most part activated by sunlight. Formaldehyde and nitrous acid, in particular, show high potential as free radical initiators during the sunrise period. After initial free radical attack, the VOC's decompose through paths resulting in the production of peroxyl radical species (HO_2, RO_2, $R'O_2$, etc.) and partially oxidized products, which in themselves may be photoactive radical-producing compounds. The peroxyl radicals react with NO, converting it to NO_2, and in the process produce hydroxyl/alkoxyl radical species (OH, RO, R'O, etc.). Alkoxyl radicals can be further oxidized, forming additional peroxyl radicals and partially oxidized products, thereby completing the inner loop reaction chain illustrated in Figure 2-4; or they may attack, as would be the major path for hydroxyl radical, the VOC pool present in the polluted atmosphere, thereby completing the outer loop reaction chain. The resultant effect in either case is the conversion of NO to NO_2 with a commensurate oxidation of reactive organic carbon, shortening of the hydrocarbon chain, and production of organic particles, CO_2 and H_2O.

The complex mixtures of organic compounds present in the polluted atmosphere react at different rates depending upon their molecular structures, resulting in varying yields of free radical species, ozone, NO_2, peroxyacetyl nitrate (PAN), and other partially oxidized organic products as a function of VOC composition and VOC-NO_x levels.

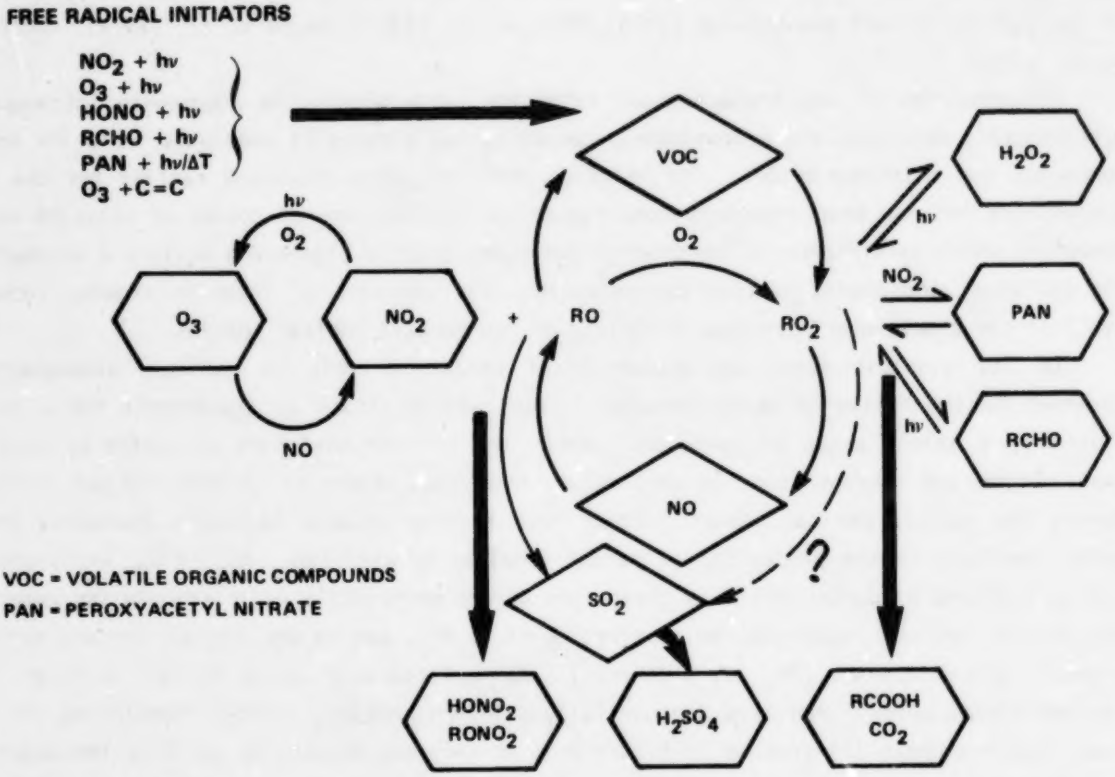
FREE RADICAL INITIATORS
NO_2 + hν
O_3 + hν
HONO + hν
RCHO + hν
PAN + hν/ΔT
O_3 +C=C
hν
O_2
O_3
NO_2
NO
+
RO
VOC
O_2
RO_2
NO
SO_2
?
H_2O_2
hν
NO_2
PAN
hν
RCHO
$HONO_2$
$RONO_2$
H_2SO_4
RCOOH
CO_2
VOC = VOLATILE ORGANIC COMPOUNDS
PAN = PEROXYACETYL NITRATE

Figure 2-4. Schematic of the polluted atmospheric photooxidation cycle.

Hydroxyl radical reactions seem to be the dominant mechanism by which CO, hydrocarbons, NO_2 and SO_2 are consumed in the atmosphere (Niki et al., 1972; Demerjian et al., 1974; Calvert et al., 1978). This highly reactive transient species, quite contrary to its organic free radical counterparts, does not show appreciable change in concentration with atmospheric VOC and NO_x variation, a result readily explainable upon review of the free radical production and consumption sources. In the case of HO, ambient concentration conditions which enhance its production tend also to consume the radical at an equivalent rate. The result is a faster cycling in the VOC-NO_x oxidation chain (i.e., increased chain lengths) but very little perturbation in the HO steady state concentration. In contrast, organic free radicals, mainly peroxyl species, are consumed by alternate pathways which are less competitive and result in increased steady state concentration.

Applying this basic knowledge of the photochemistry of the lower atmosphere, Calvert et al. (1978) determined theoretical rates of SO_2 oxidation via attack of various free radical species whose concentrations were estimated from computer simulations of the chemical reaction mechanisms for clean and polluted atmospheres.

Based on limited rate constant data for the SO_2-free radical reactions, Calvert determined that HO dominated the rate of SO_2 oxidation in the clean troposphere, while in polluted atmospheres the rate of SO_2 oxidation showed equivalent contributions from HO, HO_2, and CH_3O_2 radicals. Figure 2-5 depicts the estimated time dependent rates of SO_2 oxidation by free radical species in a polluted air mass. Recent laboratory measurements suggest that the rate of reaction of SO_2 with HO_2 and CH_3O_2 may not be as great as estimated by Calvert et al. (1978) (see discussion in Section 2.3.3.1). During July at mid-northern latitudes, typical rates of SO_2 oxidation were of the order of 1.5 percent/h and 4.0 percent/h for clean and polluted atmospheres, respectively. The major difference in rates was a result of higher concentration levels of free radicals in the hydrocarbon rich polluted atmospheres. In a similar manner, Altshuller (1979) predicted the rates of homogeneous oxidation of SO_2 to SO_4^{2-} in the clean troposphere using concentration predictions of the pertinent free radicals from a two dimensional global model by Fishman and Crutzen (1978). A sample result from this study showing the latitudinal and seasonal dependence of the rate of SO_2 oxidation is presented in Figure 2-6, the variability in rate being predominantly due to availability of ultraviolet solar intensity which drives the free-radical production process. The solar radiation dependence of SO_2 conversion rate has also been observed in field measurements within power plant plumes (Husar et al., 1978), but should be viewed cautiously in light of the complicating factors introduced by the dispersion and local chemistry of the primary source emissions.

The most important impact on SO_2 homogeneous gas phase reactions has come from recent experimental determinations of the reaction rate constants of SO_2 with HO_2 by Graham et al. (1979) and by Burrows et al. (1979) and SO_2 with CH_3O_2 by Sander and Watson (1981). As a result of these recent determinations, HO_2 and CH_3O_2 must be considered questionable as contributing sources to the oxidation of SO_2 in the atmosphere. Therefore, in the theoretical

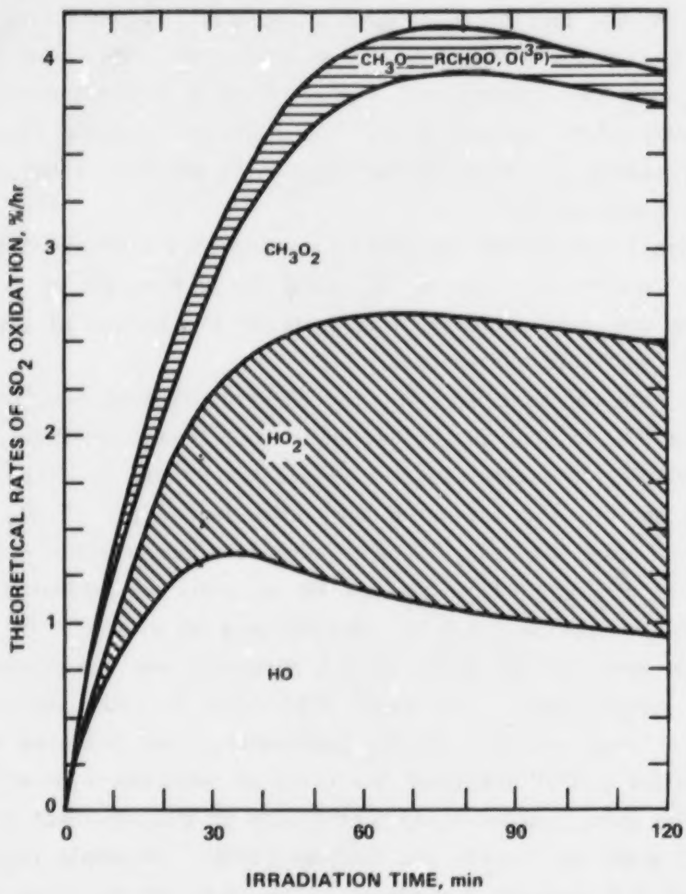

Figure 2-5. The theoretical rate of reaction (percent per hour) of various free-radical species with SO_2 is shown for a simulated sunlight-irradiated (solar zenith angle of 40°) polluted atmosphere. The initial concentrations (in ppm) were as follows: SO_2, 0.05; NO, 0.15; NO_2, 0.05; CO, 10; CH_4, 1.5; CH_2O, 0; CH_3CHO, 0. The relative humidity was 50 percent, and the temperature was 25° C.

Note: The rate constants for HO_2 and CH_3O_2 radical reactions with SO_2 are not well established. See Table 2-4 and its discussion.

Source: Calvert et al. (1978).

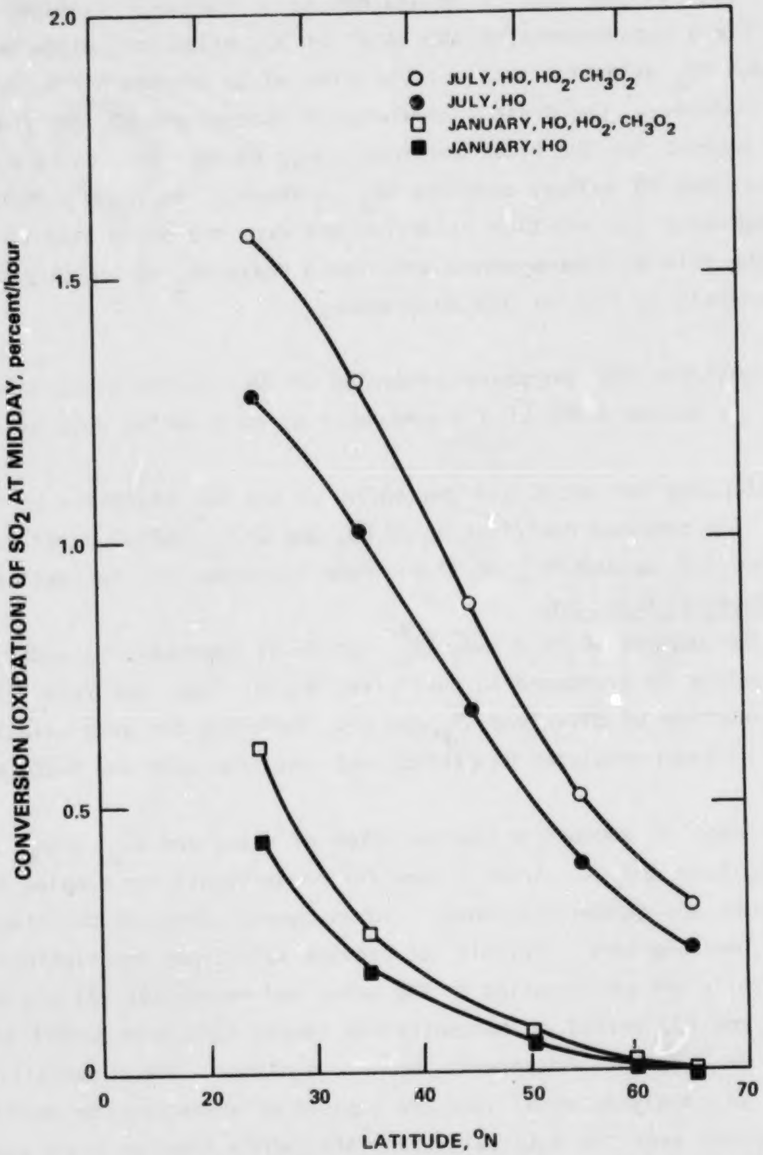

Figure 2-6. Percentage conversion at mid-day of sulfur dioxide to sulfate by HO and by HO, HO_2, and CH_3O_2 radicals as function of °N latitude in summer and winter.

Source: Altshuller (1979).

estimates of SO_2 oxidation rates, by Calvert et al. (1978), and by Altshuller (1979), only the hydroxyl radical portion of the contribution is now accepted as established, in view of these recent experimental rate constant determinations. This results in maximum established SO_2 oxidation rates of the order of 1.5 percent/h for both clean and polluted atmospheres during July at mid-northern latitudes, a factor of 2.5 less than previous theoretical estimates for polluted atmospheres. The revised rate is equivalent to a diurnally averaged rate of the order 0.4 percent/h. Field measurements on the rates of SO_2 oxidation, discussed in Chapter 6, indicate that maximum SO_2 oxidation rates of the order of 10 percent/h are typical of many atmospheric pollution scenarios. Our present knowledge of homogeneous SO_2 gas-phase reactions does not sufficiently account for the rates observed. Smog chamber studies have demonstrated that some species other than HO radical oxidizes SO_2 (Kuhlman et al., 1978; McNelis et al., 1975). Alternate homogeneous gas reaction oxidation pathways are being studied (Su et al., 1980), but certainly the role of heterogeneous and liquid phase SO_2 oxidation pathways should not be overlooked in attempts to resolve this discrepancy.

In summary:

1. HO radical dominates the gas-phase oxidation of SO_2 in the clean troposphere. A typical rate is on the order of 1.5 percent/h at noon during July at mid-northern latitudes.
2. HO radical accounts for about 1.2 percent/h of the SO_2 oxidation in the polluted troposphere. The combined contribution of HO_2 and CH_3O_2 radical reactions may be as great as about 2.8 percent/h, but their rate constants are not well established.

2.3.4 Solution-Phase Chemical Reactions

The reactions of the aqueous $SO_2 \cdot H_2O$-HSO_3^--SO_3^{2-} system is important to understanding the processes of H_2SO_4 formation in tropospheric particles, mists, fogs, and rain. This section reviews the oxidation reaction of dissolved SO_2 species, including the auto-oxidation, metal-ion catalyzed oxidation, carbon catalyzed oxidation, and reactions with the dissolved oxidants NO_2, O_3, and H_2O_2.

The state of knowledge of aqueous oxidation rates of dissolved SO_2, HSO_3^-, and SO_3^{2-} is inadequate for simple systems and is extremely poor (or nonexistent) for complex systems that include dissolved nitrogen and carbon compounds. Unfortunately, most of the studies are not definitive because the investigators: (1) did not provide sufficient descriptions of experimental procedure (especially the purification of the water and reagents), (2) did not select a proper reactor design, and (3) worked at concentration levels that were orders of magnitude greater than possible for ambient atmospheric aqueous systems. Trace quantities (at the part-per-billion level) of catalytic metal ions are capable of enhancing the reaction velocities by orders of magnitude over the auto-oxidation rate, while similar trace quantities of organics inhibit the rate. The characteristics of the chemical reactor govern the range of the half-life that can be investigated and may influence the observed rate of oxidation.

Two-phase air-water reactors (e.g., bubblers and supported droplets) may have reaction characteristics that are dependent upon: (1) the mass transfer rate of the reactants through the air-water interface, and (2) the mixing rates within the gas and water phases (Carberry, 1976; Freiberg and Schwartz, 1981). Unless an adequate characterization of the two-phase reactor was performed, it is not recommended that the implied elementary rate constant be accepted, although in many cases the results may be correct. Supported droplets may present an additional problem: radical chains are efficiently terminated at liquid-solid interfaces, thereby reducing the observed rate. Therefore, supported droplet measurements are not defensible unless it is established that the oxidation is not a free-radical mechanism. Several notable reviews of the oxidation of dissolved SO_2 and its hydration products in simple systems have been published recently (Schroeter, 1963; Hegg and Hobbs, 1978).

This review will show that:

1. The auto-oxidation (uncatalyzed) reaction is very slow compared to the other reactions.
2. Mn(II) and Fe(III) are significant catalysts for the oxidation. The kinetic rate expression is in doubt for the Mn(II) reaction, but several independent investigators agree on a rate expression for Fe(III).
3. The catalytic effectiveness of these ions is unknown: Cu(II), V(V), V(IV), Ni(II), Zn(II), and Pb(II).
4. Elemental carbon (soot) with a water film may be an effective oxidation catalyst.
5. Dissolved HNO_2 and O_3 oxidation rates are known and appear to be too low to be effective.
6. The kinetics of the dissolved H_2O_2 oxidation of dissolved SO_2 species are known and appear to be effective for forming SO_4^{2-} in particles, mists, fogs, and rain.

2.3.4.1 $S(IV)-O_2 - H_2O$ System--The simple S(IV) - O_2 auto-oxidation (see glossary) has been the subject of numerous investigations, most of which are listed in Table 2-6. The mechanism for the auto-oxidation is not firmly established. However, the behavior of the system is best explained as a modification to the scheme of Bäckström (1934), taking into account the recent results of Schmidkunz (1963) and Hayon et al. (1972):

Chain initiation

$$SO_3^{2-} + M^+ \rightarrow SO_3^- + M \qquad (2\text{-}24)$$

(M^+ = trace concentration of metal ion or reactive wall)

Chain propagation

$$SO_3^- + O_2 \rightarrow SO_5^- \qquad (2\text{-}25)$$

$$SO_5^- + SO_3^{2-} \rightarrow SO_4^{2-} + SO_4^- \qquad (2\text{-}26)$$

Oxidation

$$SO_4^- + SO_3^{2-} \rightarrow SO_4^{2-} + SO_3^- \qquad (2\text{-}27)$$

TABLE 2-6. INVESTIGATIONS OF $SO_2 - O_2$ AQUEOUS SYSTEMS

Investigators	Type of system	Comment*
Bigelow (1898)	Bubbler	1,2,3
Titoff (1903)	Bulk	2,3
Lumiere and Seyewetz (1905)	Bulk	2,3
Milbaur and Pazourek (1921)	Bulk	2,3
Reinders and Vles (1925)	2-phase bulk	1,2,3
Haber and Wansbrough-Jones (1932)	Bulk	2,3
Vol'fkovick and Belopol'skii (1932)	Bubbler	1,3
Bäckström (1934)	Theoretical	--
Fuller and Crist (1941)	Bubbler	1
Riccoboni et al. (1949)	Bulk	2,3
Abel (1951)	Theoretical	--
Winkelmann (1955)	Bulk	2
van den Heuvel and Mason (1962)	Supported droplet	1,3
Schroeter (1963)	Bubbler	1
Schwab and Strohmeyer (1965)	Bulk	2
Rand and Gale (1967)	Bulk	2,3
Scott and Hobbs (1967)	Theoretical	--
McKay (1971)	Theoretical	--
Miller and de Pena (1972)	Supported droplets	1
Brimblecombe and Spedding (1974a)	Bubbler	1
Beilke et al. (1975)	Bulk	2
Horike (1976)	Bubbler	1,3
Larson (1976)	Bubbler	1
Huss et al. (1978)	Bulk	1,3
Larson et al. (1978)	Bubbler	1

*1. Incompletely characterized 2-phase system; results may be incorrect since the investigators did not completely account for mass transfer rate or demonstrate that no concentration gradients existed.

2. Purity of water is uncertain; results cannot be considered reliable.

3. Rate expression not reported.

Termination

$$SO_4^- + \text{inhibitor} \rightarrow \text{(non-reactive species)} \tag{2-28}$$

$$\text{radical} + \text{radical} \rightarrow \text{(non-reactive species).} \tag{2-29}$$

Brimblecombe and Spedding (1974b) propose an alternative scheme that does not include the SO_4^- radical-ion; in their scheme, equation (2-26) is replaced by:

$$SO_5^- + SO_3^{2-} \rightarrow SO_3^- + SO_5^{2-} \tag{2-30}$$

$$SO_5^{2-} + SO_3^{2-} \rightarrow 2\ SO_4^{2-} \tag{2-31}$$

and equation (2-28) is absent.

Hegg and Hobbs (1978) have discussed most of the investigations identified in Table 2-6, and they summarized the rate expressions, rate constants, and important features of the studies. The observations can be classified into three types of rate expressions:

1. The type first reported by Fuller and Crist (1941),

$$\frac{d[SO_4^{2-}]}{dt} = \{k_a + k_b\ [H^+]^{0.50}\}\ [SO_3^{2-}] \tag{2-32}$$

2. The type first reported by Winkelmann (1955),

$$\frac{d[SO_4^{2-}]}{dt} = k_c\ [SO_3^{2-}] \tag{2-33}$$

3. The type observed by Beilke et al. (1975).

$$\frac{d[SO_4^{2-}]}{dt} = k_d\ [H^+]^{-0.16}[SO_3^{2-}] \tag{2-34}$$

The values that have been reported for k_a and k_b for Type 1 reaction (equation 2-32) are shown in Table 2-7. Schroeter (1963) has argued that his values obtained for air (20 percent O_2) are in excellent agreement with those obtained by Fuller and Crist (1941) for pure O_2, assuming a first-order dependence of the rate on dissolved $[O_2]$. In fact, no study has demonstrated an $[O_2]$-dependence other than zero; hence, these two studies differ by a factor of ~5.

The values reported for k_c for Type 2 reaction (equation 2-33) are shown in Table 2-8. These values, many of which were obtained by Beilke and Gravenhorst (1978) through a reanalysis of the original investigators' reported data and expressions, are in good agreement.

For Type 3 reaction (equation 2-34), Beilke et al. (1975) observed a value of $k_d = 1.2 \times 10^{-4}\ sec^{-1}M^{0.16}$ (pH = 3-6, T = 25°C). It is presently unresolved as to which type of rate expression is correct. Doubt is cast on "Type 3" found by Beilke et al. (1975) because of the

TABLE 2-7. VALUES[a] OF k_a AND k_b FOR REACTION TYPE 1

Investigator	k_a, sec^{-1}	k_b, $sec^{-1}M^{-1/2}$	pH	T,°C
Fuller and Crist (1941)	1.3×10^{-2}	6.6	5.1 - 7.8	25
Schroeter (1963)	2.9×10^{-3}	32	7.0 - 8.2	25
McKay (1971)[b]	1.3×10^{-3}	57	5.1 - 7.8	25
Larson et al. (1978)	4.8×10^{-3}	8.9	4 - 12	25

[a] Adapted from Hegg and Hobbs (1978)

[b] McKay used a more recent value for K_{40}(=6.26×10^{-8}M) in expressing k_b for Fuller and Crist's (1941) data.

TABLE 2-8. VALUES[a] OF k_c FOR REACTION TYPE 2

Investigator	k_c, sec^{-1}	pH	T,°C
Winkelmann (1955)	3.5×10^{-3}	7	25
Schroeter (1963)[b]	$\sim(6-0.6)\times10^{-3}$	7 - 8	25
Scott and Hobbs (1967)[c]	1.6×10^{-3}	~6.2 - 6.9	25
Miller and de Pena (1972)	3×10^{-3}	2 - 4	25
Brimblecombe and Spedding (1974a)[d]	$(3.7-0.6)\times10^{-3}$	4 - 6	25

[a] Adapted in part from Beilke and Granvenhorst (1978) and Hegg and Hobbs (1978).

[b] Determined by Beilke and Gravenhorst (1978) from Schroeter's (1963) data for pH = 7-8.

[c] Determined by Scott and Hobbs (1967) from Van den Heuvel and Mason (1963) data.

[d] Determined by Beilke and Gravenhorst (1978) by transforming the rate constants reported for pH = 4-6 by Brimblecombe and Spedding (1974a).

use of a plastic vessel that could have introduced trace organic inhibitors into the system. All of the other studies (yielding "Types 1 and 2") were performed with two-phase systems whose mass transfer properties were insufficiently reported.

The auto-oxidation is inhibited by trace concentrations of organic species. The classes of organic species capable of serving as inhibitors include alcohols, glycols, aldehydes, ketones, phenols, amines, and acids. Bäckström (1934) first demonstrated that the inhibition of sulfite oxidation can be expressed as:

$$\frac{d[SO_4^{2-}]}{dt} = \{A/(B + m)\}\ k_{35}\ [SO_3^{2-}] \qquad (2\text{-}35)$$

where:

k_{35} = the uninhibited rate constant
A,B = constants that are functions of the inhibitor
m = molar concentration of the inhibitor.

The influence of inhibitors on the rate has been extensively studied by Schroeter (1963), and more recently by Altwicker (1979). According to Schroeter (1963), A and B are usually on the order of 10^{-5} molar, which means that inhibitor concentrations greater than 10^{-6} molar are effective. The form of the rate equation (Equation 2-35) suggests that the mechanism involves a bimolecular reaction between an inhibitor molecule and a radical in the chain.

In summary:

1. The auto-oxidation reaction is very slow.
2. The rate is extremely sensitive to the presence of catalysts and inhibitors.
3. The rate is first order in sulfite.
4. No reaction mechanism has been satisfactorily demonstrated to account completely for the observations of the more reliable studies (e.g., the dependence of the rate on $[H^+]^{0.5}$ found by Fuller and Crist, 1941 and by Larson et al., 1978).

2.3.4.2 S(IV) - catalyst - O_2 - H_2O System--It is well established that some metal cations catalyze the oxidation of HSO_3^- and SO_3^{2-} by molecular O_2. Of particular interest to the issue of atmospheric sulfate formation in particles, mist, fog, and rain is possible catalytic activity of Mn(II), Fe(III), Cu(II), Ni(II), V(IV), and V(V). General features of the catalyzed reaction include: (a) inhibition by oxidizable organic molecules, (b) inhibition by metal ion-complexing molecules (inorganic and organic), (c) exhibition of an induction time of several seconds to several minutes, (d) detection of metal ion - S(IV) complexes, (e) no dependence of rate on dissolved O_2 concentration, and (f) dependence of the rate on the inverse of the initial H^+ concentration (i.e., the rate is independent of pH change after the reaction has been initiated). While the catalytic reaction mechanisms are unknown, they are thought to be a modification of the initiation step of the auto-oxidation free radical mechanism (Equations 2-24 through 2-29); instead of M^+ being a trace concentration ($<10^{-9}$ M) of metal ion or a reactive wall, it is a reagent present at concentrations $>10^{-6}$ M. The rate expressions for the various catalysts have different forms, suggesting different types of initiation mechanisms (e.g., simple redox reactions or the formation of stable, reactive complexes). The agreement among independent investigators is generally poor, indicating the likelihood of mass transfer limitations of the rate or the presence of contaminants. A large percentage of the investigations were conducted with two-phase reactors for which the mass transfer characteristics were not adequately reported; therefore, those results, which may be correct, are not considered for estimating the elementary rate constant and for determining the reaction order. Also, results of investigations using supported droplets may be biased due to radical chain termination at the liquid-solid interface.

The Mn(II) catalyzed reaction kinetics have been investigated for over 75 years. The studies pertinent to the formation of SO_4^{2-} in the troposphere are presented in Table 2-9. One of the first critics of Mn(II) catalysis studies was Titoff (1903), who remarked: "In Bigelow's (1898) work the reaction occurred between two phases, and the retardation could be determined by a change in the boundary layer or by a decrease in the solution rate of oxygen." Unfortunately, that comment applies to all but three of the Mn studies shown in Table 2-9, which are: Hoather and Goodeve (1934), Neytzell-de Wilde and Taverner (1958), and Coughanowr and Krause (1965). It is odd that none of these investigators presented rate expressions and rate constants derived from their data. Instead, they left to the reader the task of extracting that information. Estimates of their rate expressions are presented in Table 2-10. There is agreement that the Mn(II) catalyzed rate is independent of dissolved O_2, SO_2, HSO_3^-, and SO_3^{2-} concentrations.

Clearly, Hoather and Goodeve (1934) and Coughanowr and Krause (1965) are in agreement. However, Neytzell-de Wilde and Taverner (1958) observed a first-order dependence on [Mn(II)]. There seems to be no basis to discount any of the three investigations, yet it appears that serious errors may have been made. The results of Neytzell-de Wilde and Taverner (1958) are slightly preferred because: (1) they measured the rate of disappearance of S(IV) by direct chemical means, and (2) the period of observation (10-100 minutes) of the experimental runs were sufficiently long that it is reasonable that the rate of oxidation was measured after the establishment of the radial chains, and not during the induction period.

The Fe(III) catalyzed reaction studies that are pertinent to the formation of SO_4^{2-} in the troposphere are identified in Table 2-11. The only studies not using two-phase systems (subject to mass transport limitations) are those of Neytzell-de Wilde and Taverner (1958), Karraker (1963), Brimblecombe and Spedding (1974a), and Fuzzi (1978). Hegg and Hobbs (1978) have pointed out that Karraker (1963) did not investigate the catalyzed oxidation in which dissolved O_2 is the oxident, but instead investigated the redox system associated with the couple $Fe(III) + e^- \rightarrow Fe(II)$ in an oxygen-free system. Thus, Karraker's work is not applicable. Neytzell-de Wilde and Taverner (1958) reported that the SO_4^{2-} formation rate was second order for [S(IV)], but Karraker (1963) has reanalyzed their data and has shown instead that

TABLE 2-9. INVESTIGATIONS OF SO_2 - MANGANESE - O_2 AQUEOUS SYSTEM

Investigators	Type of System	Comment*
Titoff (1903)	Bulk	2
Johnstone (1931)	Bubbler	1,2
Hoather and Goodeve (1934)	Bulk	2
Bassett and Parker (1951)	Bulk	2
Johnstone and Coughanowr (1958)	Supported droplet	1,2
Neytzell-de Wilde and Taverner (1958)	Bulk	2
Johnstone and Moll (1960)	Free droplets	2
Coughanowr and Krause (1965)	Bulk and flow	2
Bracewell and Gall (1967)	Bubbler	1
Matteson et al. (1969)	Free and supported droplets	3
Cheng et al. (1971)	Supported droplets	1

*1. Incompletely characterized 2-phase system; results may be incorrect since the investigators did not completely account for mass transfer rate or demonstrate that no concentration gradients existed.

2. Rate expression not reported.

3. Results are biased due to continued reaction of (supported) droplets on filter of sampler; rate expression cannot be considered reliable.

TABLE 2-10. RATE EXPRESSION FOR THE MANGANESE-CATALYZED OXIDATION

Expression[a,b,c]	pH	Investigators
$\frac{d[SO_4^{2-}]}{dt} \cong 44\ [Mn(II)]^{1.7}\ [S(IV)]^0\ [H^+]^0$	3-4	Adapted from Hoather and Goodeve (1934)
$\frac{d[SO_4^{2-}]}{dt} \cong 1.7 \times 10^{-5}\ [Mn(II)]\ [S(IV)]^0\ [H^+]_0^{-1}$	~2.2	Adapted from Neytzell-de Wilde and Taverner (1958)
$\frac{d[SO_4^{2-}]}{dt} \cong 8\ [Mn(II)]^2\ [S(IV)]^0$	~3-4	Adapted from Coughanowr and Krause (1965); dependence on pH not reported

a. The units are: liter, mole, second.

b. Concentrations shown with zero power (e.g., $[S(IV)]^0$) indicate that the investigators found the rate to be independent of those species. Note that any concentration to the zero power is equal to unity.

c. The term $[H^+]_0^{-1}$ indicates that the rate is dependent only on the inverse of the initial H^+ ion concentration; changes in H^+ concentration after the reaction is in progress do not affect the rate.

TABLE 2-11. INVESTIGATIONS OF SO_2 - IRON - O_2 AQUEOUS SYSTEM

Investigators	Type of System	Comment*
Reinders and Vles (1925)	Bulk	2
Bassett and Parker (1951)	Bulk	2
Higgins and Marshall (1957)	Bulk	2
Johnstone and Coughanowr (1958)	Support droplet	1
Junge and Ryan (1958)	Bubbler	1,2
Neytzell-de Wilde and Taverner (1958)	Bulk	2
Johnstone and Moll (1960)	Free droplets	2
Danilczuk and Swinarski (1961)	Bulk	2
Karraker (1963)	Bulk	3
Bracewell and Gall (1967)	Bubbler	1
Brimblecombe and Spedding (1974a)	Bubbler	1
Brimblecombe and Spedding (1974b)	Not reported	4
Freiberg (1974)	Theoretical	--
Lunak and Veprek-Siska (1975)	Flow	5
Barrie and Georgii (1976)	Supported droplet	1
Fuzzi (1978)	Bulk	--

*1. Incompletely characterized 2-phase system; results may be incorrect since the investigators did not completely account for mass transfer rate or demonstrate that no concentration gradients existed.

2. Rate expression not reported.

3. O_2-free system; results not applicable to tropospheric SO_2 oxidation.

4. Insufficient details reported to determine if the results should be considered reliable.

5. Photochemical initiation.

the order is unity. Neytzell-de Wilde and Taverner (1958) did not present a rate expression and constant for the Fe(III) system. An estimate derived from their paper is presented in Table 2-12. Brimblecombe and Spedding (1974a) reported a rate expression and constant measured at a constant pH = 4; unfortunately, they used a plastic reaction vessel, which could have released organic inhibitors into the system, causing the rate to be diminished. (At pH = 4, their rate is 0.25 of that of Neytzell-de Wilde and Taverner, 1958, and 0.1 of that of Fuzzi, 1978.) Fuzzi (1978) did not note the similarity of his observations to those of Neytzell-de Wilde and Taverner (1958), especially the dependence of the rate on the initial inverse H^+ concentration for pH $\leq$ 4.0. Fuzzi's (1978) rate expression has been modified by incorporating the dependence on $[H^+]_0^{-1}$ and is presented in Table 2-12. Note that Fuzzi's (1978) modified rate constant is 2.5 times greater than that of Neytzell-de Wilde and Taverner (1958), which is good agreement for this type of measurement; these two studies appear to be definitive for the Fe(III) system, and there is no basis to prefer one over the other. Fuzzi (1978) has clearly domonstrated the change in the reaction order of [S(IV)] from 1 to 2 as pH increases from 4 to 5. The change in kinetics is due to the formation of colloidal $Fe(OH)_3$ for pH > 4, which provides an explanation for the disagreement among earlier investigators. Because of the formation of the $Fe(OH)_3$ colloid, it is unlikely that a meaningful Fe(III) catalyzed rate expression for use in tropospheric sulfate formation can be stated for conditions in which pH > 4.

TABLE 2-12. RATE EXPRESSION FOR THE IRON-CATALYZED OXIDATION

Expression[a,b]	pH	Investigators
$\frac{d[SO_4^{2-}]}{dt} \cong 0.04\ [Fe(III)]\ [S(IV)]\ [H^+]_0^{-1}$	~2	Adapted from Neytzell-de Wilde and Taverner (1958)
$\frac{d[SO_4^{2-}]}{dt} = 100\ [Fe(III)]\ [S(IV)]$	4	Adapted from Brimblecombe and Spedding (1974a)
$\frac{d[SO_4^{2-}]}{dt} \cong 0.1\ [Fe(III)]\ [S(IV)]\ [H^+]_0^{-1}$	≤ 4	Adapted from Fuzzi (1978)

[a] The units are: liter, mole, second.

[b] The term $[H^+]_0^{-1}$ indicates that the rate is dependent on the inverse of the initial H^+ ion concentration; changes in H^+ concentration after the reaction is in progress do not affect the rate.

The Cu catalyzed reaction kinetics have been described in the early work of Titoff (1903). The pertinent investigations are identified in Table 2-13. As with the Mn and Fe studies, most of the Cu studies were performed with incompletely characterized systems. Fuller and Crist (1941) point out that the prior work is unreliable because of the likely presence of contaminants. However, the investigations of Fuller and Crist (1941) were carried out in a two-phase reactor whose mass transfer characteristics were not completely described; no one since has conducted a more definitive study of this stystem. The reagent concentrations used by Barron and O'Hern (1966) are orders of magnitude too large, and the pH range (>8) used by Mishra and Srivastava (1976) is not applicable. For that reason, no rate expression can be recommended as reliable for use in calculating sulfate formation rates due to Cu catalysis in the troposphere. Also, because of interference from the electric motors in sampling devices, reported airborne Cu concentrations may be unreliable (Patterson, 1980).

Vanadium catalysis has been reported in only one study (Bracewell and Gall, 1967); a bubble reactor was used, and its mass transfer characteristics were inadequately reported. Therefore, no rate expression can be recommended as reliable. However, Bracewell and Gall (1967) did observe qualitatively that V(V) was orders of magnitude less effective than Mn and Fe; unfortunately, they did not study V(IV). It is likely that V(V) catalysis is unimportant for sulfate formation in the troposphere. There are also no definitive studies for Cr(III), Ni(II), Zn(II), and Pb(II), but from the qualitative work of Bracewell and Gall it appears that these catalytic reactions are unimportant.

Barrie and Georgii (1976) have demonstrated qualitatively that Mn(II) and Fe(III) exhibit a synergistic rate for the catalysis of S(IV) oxidation. Their rate expression cannot be considered reliable, since they use a supported droplet.

In summary:

1. S(IV) oxidation rates are significantly increased by Mn(II) and Fe(III). There is serious doubt regarding the rate expression for Mn(II), but the agreement among independent studies is much better for Fe(III).
2. These systems are presently inadequately characterized: Cu(II), V(V), Ni(II), Zn(II), Pb(II), and Cr(III). No studies of V(IV) have been reported.
3. There are no quantitative studies of metal ion-metal ion synergism.
4. The ability of atmospheric organic compounds to inhibit the catalysis is unknown.
5. All studies have been performed in the absence of HCO_3^-; however, the reactions

   $$SO_4^- + HCO_3^- \rightarrow HCO_3 + SO_4^{2-}$$

   $$HO + HCO_3^- \rightarrow HCO_3 + OH^-$$

   may be important. It is possible that such reactions may occur, and if so, they would prevent the oxidation radical chain from establishing, since HCO_3 is not a powerful oxidizer (Hoigné and Bader, 1978).
6. In general, the rate expressions for catalytic oxidation to form H_2SO_4 are not well established.

TABLE 2-13. INVESTIGATIONS OF SO_2 - COPPER - O_2 AQUEOUS SYSTEMS

Investigators	Type of System	Comment*
Titoff (1903)	Bulk	2
Reinders and Vles (1925)	Bulk	2
Alyea and Bäckström (1929)	Bulk	2
Johnstone (1931)	Bubbler	1
Albu and von Schweinitz (1932)	Bulk	2
Fuller and Crist (1941)	Bubbler	1
Riccoboni et al. (1949)	Bulk	2
Bassett and Parker (1951)	Bulk	2
Higgins and Marshall (1957)	Bulk	2
Johnstone and Coughanowr (1958)	Supported droplet	1
Junge and Ryan (1958)	Bubbler	1
Barron and O'Hern (1966)	Flow	--
Bracewell and Gall (1967)	Bubbler	1
Cheng et al. (1971)	Supported droplet	1
Veprek-Siska and Lunak (1974)	Flow	2
Barrie and Georgii (1976)	Supported droplet	1
Huss et al. (1978)	Bulk	2
Mishra and Srivastava (1976)	Flow	--

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*1. Incompletely characterized 2-phase system; results may be incorrect since the investigators did not completely account for mass transfer rate or demonstrate that no concentration gradients existed.

2. Rate expression not reported.

2.3.4.3 S(IV) - Carbon Black - O_2 - H_2O--The catalysis of the oxidation of dissolved SO_2 by carbon particles suspended in the water has been studied by Chang et al. (1979) and by Eatough et al. (1979). It was found by Chang et al. (1979) that the oxidation rate of dissolved SO_2 species was:

$$-\frac{d[S(IV)]}{dt} = k_{36}[C]\,[O_2]^{0.69}[S(IV)]^0 \exp(-E_a/RT) \qquad (2\text{-}36)$$

with an activation energy of E_a = 11.7 kcal/mol over the pH range of 1.45 to 7.5 for the carbon studied, which was Nuchar-190. (The investigators demonstrated that Nuchar-190 behaved similarly to soot from acetylene and natural gas flames.) An average value of $k = 1.17 \times 10^5$ $mol^{0.3} \times liter^{0.7}$/g-sec was reported. The rate-limiting step has been suggested to be the formation of an activated complex between molecular oxygen and the carbon surface (Chang et al., 1979; Eatough et al., 1979).

Chang et al. (1979) have estimated that for 10 µg of their fine carbon soot suspended in 0.05 g of liquid water and dispersed in 1 m^3 of air, the atmospheric sulfate production would be about 1 µg/hr. Heavy hydrocarbons are adsorbed on the surfaces of atmospheric soots and may inhibit the carbon-surface catalyzed oxidation of dissolved SO_2. At this time, it remains to be demonstrated that the laboratory soots used by Chang et al. (1979) correspond to those present in the atmosphere or that the suspension of soot at ambient levels (<10 µg/m^3) in aerosols, cloud droplets, or rain is similar to the laboratory system.

2.3.4.4 S(IV) - Dissolved Oxidants - H_2O--Hydrogen peroxide, O_3 and NO_2 may be important in the oxidation of SO_2 in aqueous aerosols and fogs. These compounds are not highly reactive with SO_2 in air, but their reactivity is enhanced in the liquid phase. Again, caution is advised in accepting the results of studies of two-phase systems in which the investigators have not completely accounted for the possibility of the mass transport limitation of the oxidation rate. Therefore, only the recent results for single-phase systems are discussed here.

Martin et al. (1981) used a stopped-flow reactor to investigate the kinetics of oxidation of aqueous SO_2 species by aqueous NO, NO_2^-, and NO_3^-. Over the pH range of 0.6 to 3.2, they found for NO and NO_3^- that the disappearance of S(IV) species is:

$$-\frac{d[S(IV)]}{dt} = k_{37}[NO \text{ or } NO_3^-]\,[S(IV)] \qquad (2\text{-}37)$$

$$k_{37} \leq 0.01 \text{ mole } l^{-1}s^{-1}.$$

However, for the same conditions, the reaction with NO_2^- is rapid and the formation of SO_4^{2-} can be expressed as:

$$\frac{d[SO_4^{2-}]}{dt} = k_{38}[H^+]^{0.5}\,[HNO_2 + NO_2^-]\,[SO_2\cdot H_2O + HSO_3^-] \qquad (2\text{-}38)$$

$$k_{38} = 142 \text{ (liter/mole)}^{1.5}s^{-1}$$

The NO_2^- is reduced quantitatively in this reaction to N_2O. Martin et al. (1981) also observed that this reaction is not catalyzed by Fe(III), Mn(II), or VO^{2+}. It is unlikely that tropospheric HNO_2 concentrations are high enough for this reaction to be important for H_2SO_4 formation.

The oxidation of dissolved SO_2 by O_3 has been investigated with stopped-flow systems. Penkett (1972) and Penkett et al. (1979) have interpreted their work in terms of a decomposition of O_3 to initiate a free-radical chain reaction involving OH, HSO_3, and HSO_5 radicals, after Bäckström (1934). Penkett et al. (1979) suggested that the rate expression is

$$\frac{d[SO_4^{2-}]}{dt} \cong k_{39}[HSO_3^-]\,[O_3]\,[H^+]^{-1} \qquad (2\text{-}39)$$

where $k_{39} \cong 71\ sec^{-1}$. Erickson et al. (1977) reported the fractional contributions of the oxidation of the three sulfur oxide species by ozone at various pH values; their rate expressions are:

$$\frac{d[SO_4^{2-}]}{dt} = k_{40}[SO_2 \cdot H_2O]\,[O_3] \qquad (2\text{-}40)$$

$$\frac{d[SO_4^{2-}]}{dt} = k_{41}[HSO_3^-]\,[O_3] \qquad (2\text{-}41)$$

$$\frac{d[SO_4^{2-}]}{dt} = k_{42}[SO_3^{2-}]\,[O_3] \qquad (2\text{-}42)$$

where k_{40} = 590 liter/mol·sec, $k_{41} = 3.1 \times 10^5$ liter/mol·sec, and $k_{42} = 2.2 \times 10^9$ liter/mol·sec.

Penkett et al. (1979) used a stopped-flow reactor to determine the kinetics of oxidation of dissolved SO_2 species by H_2O_2. It was found that the rate of sulfate formation is given by:

$$\frac{d[SO_4^{2-}]}{dt} = k_{43}[H_2O_2]\,[HSO_3^-]\,[H^+] + k_{43a}[H_2O_2]\,[HSO_3^-]\,[HA] \qquad (2\text{-}43)$$

where $k_{43} \cong 2.6 \times 10^7\ liter^2/mol^2 \cdot sec$, with k_{43} and k_{43a} being the third-order rate constants for the catalysis by hydronium ions and proton-donating buffers (HA), respectively. At $pH \leq 4$, it is found that $k_{43}/k_{43a} \geq 3200$. Therefore, the second term is probably not important for acid aerosols and fogs. It is of great significance that the reaction rate increases as the solution becomes more acidic, which is in contrast to aqueous oxidation by metal ions and by O_3. The activation energy and the effect of ionic strength on the reaction have been measured by Penkett et al. (1979). Dasgupta (1980) has criticized the presentation of Penkett et al. (1979); use of the rate expression (Equation 2-43) takes into account Dasgupta's (1980) points. Martin and Damschen (1981) have found that:

$$\frac{d[SO_4^{2-}]}{dt} = k_{44}[H_2O_2]\,[SO_2 \cdot H_2O]/\{0.1 + [H^+]\} \qquad (2\text{-}44)$$

where $k_{44} = 7.2 \times 10^4 s^{-1}$; their expression is applicable over the range $0<pH<5$ and is in good agreement with Penkett et al. (1979).

In summary:

1. The oxidation rates are known for NO and NO_3^- and are too low to be important.
2. The oxidation rate is known for NO_2^-, but the tropospheric concentration of HNO_2 is probably too low for this reaction to be important.
3. The oxidation rate is known for O_3, but it is expected to be usually unimportant.
4. The oxidation rate for H_2O_2 is known and appears to be an effective reaction for formation of H_2SO_4 in the troposphere. Possibly, this rate could be enhanced by metal ions, but no studies have been reported. Also, there are at this time no adequate data on H_2O_2 concentrations in the lower troposphere.
5. Organic oxidizers may be important, but no studies have been reported.

2.3.4.5 The Influence of Ammonia--It has been recognized for several decades that NH_3 may influence the formation rate of H_2SO_4 in aqueous particles, mist, fog, and rain. Hegg and Hobbs (1978) have reviewed the studies of the NH_3 influence and have called attention to a misunderstanding in the literature: NH_3 is commonly reported incorrectly to be a "positive catalyst" for the oxidation of dissolved SO_2. In the strict sense of the definition of "catalyst," the term cannot be applied to the role of NH_3. The observed enhancement by NH_3 of the oxidation rates of the auto-oxidation, metal-ion oxidation, and the O_3 oxidation is due to its action to raise and maintain a high pH. The following process occurs to raise and maintain a higher pH through the conversion of NH_3 to NH_4^+:

1. Ambient gaseous $HN_{3(g)}$ dissolves in the water,

$$NH_{3(g)} \rightleftarrows NH_{3(aq)} \qquad (2\text{-}45)$$

2. The dissolved $NH_{3(aq)}$ reacts with H^+, which raises the pH

$$NH_{3(aq)} + H^+ \rightleftarrows NH_4^+. \qquad (2\text{-}46)$$

Therefore, the ambient pathways of auto-oxidation, Mn(II)- and Fe(III)-catalyzed oxidation, and O_3 oxidation would have their rates enhanced by absorption of NH_3. However, the ambient pathways of H_2O_2 and HNO_2 would have their rates retarded by NH_3 absorption. The rate for soot would not be influenced.

NH_3 can play other important roles. Reinders and Vles (1925) observed qualitatively that Cu(II) was complexed by NH_3 and rendered noncatalytic. At hign pH's (>9) where $NH_{3(aq)}$ is the dominant form, NH_3 may be oxidized by O_3 and free-radicals (Hoigne and Bader, 1978).

In summary, the role of NH_3 is explained in terms of its influence on the pH of the water system; NH_3 is not a catalyst.

2.3.5 Surface Chemical Reactions

Industrial emissions of solid particles (e.g., fly ash) and fugitive dust (e.g., wind-blown soil and minerals) provide a solid-surface that may chemisorb SO_2 and yield sulfate ions. This section will review investigations of the SO_2 oxidation on the surfaces of metal oxides, fly ash, charcoal, and soot. Reaction kinetics have not been reported, but two general types of processes have been recognized: a capacity-limited reaction for SO_2 removal and a catalytic SO_2 oxidation process. The initial contact of SO_2 with the solid produces a rapid loss of SO_2 from the gas phase; the reaction rate decreases with time. For the capacity-limited reaction, the rate slowly approaches zero; for the catalytic precess, the rate levels off for a time and then approaches zero. The latter phenomenon is attributed to a pH decrease caused by H_2SO_4 formation.

Urone et al. (1968) and Smith et al. (1969) found a number of solids to be effective in removing SO_2. In Urone's studies, SO_2 was admitted to a flask containing a powder that was allowed to react with no mixing, and the product and remaining SO_2 were determined. Only the average reaction rates can be calculated from these experiments; more importantly, with this experimental procedure the rates may be diffusion-limited. The highest rate determined was for SO_2 with Fe_2SO_3; the value was >75 percent per minute. Other materials found to be slightly less reactive than Fe_2SO_3 were Fe_3O_4, PbO, PbO_2, CaO, Al_2O_3. The rate for the ferric oxide experiment was for 20 mg of Fe_2O_3 in a 2-liter flask; the Fe_2O_3 concentration would thus be 10^7 $\mu g/m^3$. Assuming a direct proportionality between rate and particle concentration, the SO_2 removal rate in the atmosphere would be calculated to be 0.04 percent per hour for 100 $\mu g/m^3$ of particles with the same reactivity as ferric oxide. However, since the mass transfer characteristics of the reactor were not reported, these results cannot be considered reliable for estimating rates.

Smith et al. (1969) did not focus on sulfate formation kinetics; instead, they illustrated through a novel experiment the ability of solid particles to adsorb SO_2 and to release SO_2 during passage through a tube with a wall that adsorbs SO_2. They measured the number of SO_2 monolayers absorbed on suspended Fe_3O_4 as a function of SO_2 partial pressure. The monolayer coverage data reported in their Table I are in error by a factor of 100 too large; e.g., the number of monolayers at 1.13 ppm should be 0.38×10^2.

Chun and Quon (1973) measured the reactivity of Fe_2O_3 to SO_2, using a flow system involving a filter containing suspended particles. They determined a removal rate constant of 9.4×10^{-3} ppm^{-1} min^{-1} ($-d\ln \theta/dt$), where θ is the fraction of surface sites available for reaction. Extrapolating this to an atmospheric particle concentration of 100 $\mu g/m^3$ with an equivalent reactivity and an SO_2 concentration of 0.1 ppm (260 $\mu g/m^3$), the data project an atmospheric removal rate of 0.1 percent per hour.

Stevens et al. (1978) report total iron concentrations in six U.S. cities ranging between 0.5 and 1.3 $\mu g/m^3$. Other species such as manganese, copper, or vanadium had total concentrations usually below 0.1 $\mu g/m^3$. Thus actual ambient air concentrations are approximately

1/50th those assumed by the authors in the above papers. A reactive particle concentration of 2 $\mu g/m^3$ would yield a predicted SO_2 removal rate of no more than 0.002 percent per hour. Therefore, surface reactions are probably not important except in sources prior to or immediately after emission.

The most comprehensive studies to date on SO_2 removal by pure solids were made by Siegel et al. (1974) and Judeikis et al. (1978). A tubular flow reactor, in which solids were supported on an axial cylinder, was used to measure reactivities of MgO, Fe_2O_3, Al_2O_3, MnO_2, PbO, NaCl, charcoal, and fly ash. They found that the rates of SO_2 removal diminished with exposure until the solids completely lost ability to react with SO_2. The relative humidity was important in determining the total capacity for SO_2 removal, but not the initial rate of uptake; total capacity increased as relative humidity increased. The capacity for SO_2 could be extended by exposure to NH_3. This type of behavior is consistent with the formation of H_2SO_4 on the surfaces.

Because carbonaceous matter is so common in ambient air particulate samples, various studies have been made of the SO_2 removal rate by carbon. A comparison of the results is difficult because of the varieties of carbon available for study, such as activated charcoal, graphite, acetylene flame products, and combustion products of diesel oil and heating oil. In regard to investigations that deal with the gas-solid reaction of SO_2 with carbon, Novakov et al. (1974) performed laboratory experiments that showed that graphite and soot particles oxidize SO_2 in air. The soot exposed to humidified air produced more SO_4^{2-} than that exposed only to dry air. For downtown Los Angeles, they observed a strong correlation between concentrations of ambient carbon and SO_4^{2-}, which supports their hypothesis that carbon (soot) oxidation of SO_2 is the major pathway for SO_4^{2-} formation (see Section 2.3.4.3).

Tartarelli et al. (1978) studied the interaction of SO_2 with carbonaceous particles collected from the flue ducts of oil-burning power stations. They concluded that the amount of adsorption is increased by the presence of oxygen and water in the gas stream. Reaction rates were not determined in this study.

Liberti et al. (1978) studied the absorption and oxidation of SO_2 on various particles, including soot from an oil furnace and various atmospheric particulate samples. They concluded that the main interaction between the SO_2 and PM is adsorption, with most catalytic reactions occurring at high temperatures, near the combustion source. Their experiments with atmospheric particulate samples led them to the conclusion that any heterogeneous nonphotochemical sulfate formation is strongly dependent on the reactivity of the particle surface, and hence the history (aged, freshly emitted), of the aerosol.

In summary:

1. Surface reactions are capacity-limited. Those that involve catalysis in liquid films can be extended by the absorption of NH_3.
2. The initial rates may be large, but quickly approach zero.

3. Except for the carbon (soot) reaction, solid surface reactions do not seem to be effective pathways for H_2SO_4 formation in the troposphere.

2.3.6 Estimates of SO_2 Oxidation

At this point it is interesting to compare the rates of SO_2 oxidation by the more important reactions identified in the previous sections of this chapter. The important reactions for gas-phase and aqueous-phase oxidation are listed in Table 2-14, and rates of SO_2 oxidation for an assumed set of conditions are present. These calculations ignore the nonhomogeneous nature of the troposphere and assume that all of the reactants are well mixed. (The more general case is treated in Chapter 6.)

TABLE 2-14. ESTIMATES OF SO_2 OXIDATION RATES IN WELL-MIXED TROPOSPHERE

Reaction	Rate, % h^{-1}			Discussion Section	Comments*
I. Gas Phase					
HO radical	0.3 - 1.3			2.3.3.2	a
HO_2 radical	0.4 - 2.0			2.3.3.2	a,b
CH_3O_2 radical	0.3 - 1.5			2.3.3.2	a,b
II. Aqueous Phase, pH:	1	3	5		
Mn(II) catalysis	1E-1	1E+1	1E+3	2.3.4.2	b,c,d,i
Fe(III) catalysis	5E-5	5E-1	5E+3	2.3.4.2	c,e,i
C (soot) catalysis	3E+1	3E+1	3E+1	2.3.4.3	f,i
O_3 (40 ppb)	2E-8	2E-6	2E-4	2.3.4.4	c,g
O_3 (120 ppb)	6E-8	6E-6	6E-4	2.3.4.4	c,g
H_2O_2 (1 ppb)	2E-2	3E-2	3E-2	2.3.4.4	c,h
H_2O_2 (10 ppb)	2E-1	2E-1	3E-1	2.3.4.4	c,h

NOTE: "E" denotes "exponent to the base 10" (e.g., 3E-1 = 3×10^{-1})

*

a. Typical range for daytime at northern midlatitudes during the summer.

b. This reaction rate is not well established; see discussion section.

c. Assumed that liquid water volume of aerosol = $50 \times 10^{-12} m^3/m^3$, $[SO_2]_g$ = 10 ppb (or 26 $\mu g/m^3$).

d. Assumed that Mn(II) mass concentration = 20 ng/m^3; also, the Mn(II) is assumed to be uniformly dissolved in the liquid water of the aerosol ([Mn(II)] = 8.9×10^{-3} M). Rate calculation used the expression of Neytzell-de Wilde and Taverner (1958); see Table 2-7.

e. Assumed that Fe(III) mass concentration = 2 $\mu g/m^3$; also, the Fe(III) is assumed to be uniformly dissolved in the liquid water of the aerosol ([Fe(III)] = 0.9 M). Rate calculation used the expression of Neytzell-de Wilde and Taverner (1958); see Table 2-9.

f. Assumed that C mass concentration = 10 $\mu g/m^3$ and behaves as the soots studied by Chang et al. (1979), whose expression was used for this calculation (Equation 2-36).

g. Rate calculation was based on Equation 2-39.

h. Rate calculation was based on Equation 2-43.

i. Influence of inhibitors has been ignored, but they are likely to suppress the rate by orders of magnitude.

For this comparison, it has been assumed that the SO_2 concentration is 10 ppb (26 $\mu g/m^3$) for all of the reactions and the liquid water content of the aerosol is 50×10^{-12} m^3/m^3.

The gas-phase rates were calculated from the material in Section 2.3.3.2, while the aqueous-phase rates were derived from Sections 2.3.4.2-4. Unbased assumptions include:

1. The ambient mass concentration of 20 ng/m^3 for Mn is reasonable, but: (a) it is not known if the predominant form is Mn(II), and (b) it is unlikely that Mn is uniformly distributed and dissolved. Inhibitors have been ignored, but they likely suppress the rate by orders of magnitude.
2. Likewise, the ambient concentration of 2 $\mu g/m^3$ for Fe is reasonable, but: (a) it is not known if Fe(III) is the predominant form, and (b) it is unlikely that Fe is uniformly distributed and dissolved. Inhibitors have been ignored, but they likely suppress the rate by orders of magnitude.
3. There is no basis to assume that the rate equation observed for laboratory-generated carbon (soot) applies to atmospheric carbon. Inhibitors may be important.
4. The rates for the HO_2 and CH_3O_2 reactions recommended by Calvert et al. (1978) are not well established.

It is very likely that the inhibitor-free rates estimated for Mn(II) catalysis, Fe(III) catalysis, and C (soot) catalysis are gross overestimates. Also, the HO_2 and CH_3O_2 rates may be too high.

Uncritically accepting all of the rates, at a pH = 3, and $[H_2O_2]$ = 10 ppb, the SO_2 conversion rate would exceed 40 percent/h. However, if only the well-established rates are considered, the SO_2 conversion rate becomes ~1.1 percent/h.

In summary:

1. The gas-phase reaction rate of HO and the aqueous-phase reaction of H_2O_2 are well established, but are expected to account for only about 1.1 percent/h (under the conditions given in Table 2-14).
2. The Mn(II), Fe(III), and C (soot) catalyzed reactions have sufficient rates to dominate SO_2 oxidation in the troposphere, but the assumptions discussed above may not be reasonable.

2.4 PHYSICS AND CHEMISTRY OF PARTICULATE MATTER

Knowledge of the physics and chemistry of particulate matter is necessary for design of satisfactory samplers and monitors, understanding the relationships between sources and effects, and understanding important processes in the troposphere that involve chemical transformations and removal.

In Section 2.2, the global cycle and annual budget for sulfur were presented to aid in establishing the goals and limitations of this document's treatment of sulfur oxides. That discussion is incomplete, in that particulate matter is related to cycles of numerous elements and their interactions. Among the most important cycles of elements are: sulfur, nitrogen, carbon, hydrogen, boron, oxygen, sodium, aluminum, silicon, phosphorous, chlorine, potassium, calcium, vanadium, manganese, iron, mercury, and lead. Since it is beyond the scope of this document to deal with the details of these cycles, a perspective can be obtained form a budget estimate of the particulate mass injected into the troposphere. The estimate by Hidy and Brock (1971) of the daily particulate mass emitted or formed in the troposphere is presented in Table 2-15. Globally, the anthropogenic contribution is about 6 percent; however, the nonhomogeneous distribution and the type of emissions pose serious problems. (See Chapter 4 for a discussion of sources in the United States.) Figure 2-2 showed the general interrelations of pathways, processes, and properties of sulfur oxides and particulate matter and effects. Section 2-3 treated the SO_2 physical properties and chemistry (including transformation chemistry), which are indicated in Figure 2-2. Section 2.4 will discuss the physics and chemistry of particulate matter that are related to particle properties, single-particle dynamics of motion, formation and growth, and aerosol system dynamics.

The budget in Table 2-15 indicates that secondary particulate matter formation dominates the rates. This important source will be discussed in Section 2.4.

2.4.1 Definitions

Aerosol science spans chemistry, physics, engineering, meteorology, and the biological sciences. Unfortunately, the lack of communication among workers in these diverse disciplines has impeded the unification of their ideas. One of the results has been a lack of universally accepted definitions of the terms "aerosol" and "particle" and the terms for classification of aerosol systems. The definitions used here are consistent with general usage by atmospheric scientists.

Particle: Any object having definite physical boundaries in all directions, without any limit with respect to size (Cadle, 1975). In practice, the particle size range of interest is used to define "particle." In atmospheric sciences, "particle" usually means a solid or liquid subdivision of matter that has dimensions greater than molecular radii (~10 nm); there is also not a firm upper limit, but in practice it rarely exceeds 1 mm.

Aerosol: A disperse system with a gas-phase medium and a solid or liquid dispersed phase (Fuchs, 1964). Often, however, individual workers modify the definition of "aerosol" by arbitrarily requiring limits on individual particle motion or surface-to-volume ratio (e.g., see Hidy and Brock, 1970). Aerosols are formed by (a) the suspension of particles due to grinding or atomization, or (b) condensation of supersaturated vapors (Fuchs, 1964).

An aerosol is not the halocarbon vapor used as the propellant in pressured cans (commonly referred to as "aerosol cans" and "aerosol bombs"). Improper use of the term "aerosol" by marketers of foams, gels, sprays, etc., has caused the lay public to associate incorrectly environmental issues of suspended particulate matter with the issue of halocarbon impact on the stratospheric ozone layer. In the context of this document, the term "aerosol" is not related to the impact of halocarbons on the stratospheric ozone layer.

TABLE 2-15. ESTIMATE OF GLOBAL TROPOSPHERIC PARTICULATE MATTER PRODUCTION RATES[a]

Source	% by Weight of Total[b]
A. Natural Sources	
1. Primary	
Windblown dust	9.3
Sea Spray	28
Volcanoes	0.09
Forest Fires	3.8
2. Secondary	
Vegetation	28
Sulfur Cycle	9.3
Nitrogen Cycle	14.8
Volcanoes (gases)	0.009
SUBTOTALS:	93
B. Manmade Sources	
1. Primary	
Combustion and Industrial	2.8
Dust from Cultivation	0.009
2. Secondary	
Hydrocarbon Vapors	0.065
Sulfates	2.8
Nitrates	0.56
Ammonia	0.028
SUBTOTALS:	6
TOTAL:	99[c]

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[a] Source: Hidy and Brock (1971)

[b] Production rate = 10.7×10^6 metric tons/day

[c] Not 100% because of round-off errors.

Traditionally, workers in various scientific fields have classified the aerosol systems to reflect their origin, physical state, and range of particle size. The meanings of these classifications are not universally accepted; however, the following definitions are consistent with general usage by atmospheric scientists.

Particulate Mass: A generic classification in which no distinction is made on the basis of origin, physical state, and range of particle size (Dennis, 1976). (The term "particulate" is an adjective, but often it is incorrectly used as a noun.)

Dust: Dispersion aerosols with solid particles formed by comminution or disintegration, without regard to particle size (Fuchs, 1964; Dennis, 1976; Hidy and Brock, 1970). Typical examples include (a) natural minerals suspended by the action of wind, and (b) solid particles suspended during industrial grinding, crushing, or blasting.

Smokes: Dispersion aerosols containing both liquid and solid particles formed by condensation from supersaturated vapors (Fuchs, 1964; Hidy and Brock, 1970). Generally, the particle size is in the range of 0.1 μm to 10 μm. A typical example is the formation of particles due to incomplete combusion of fuels.

Fumes: Condensation aerosols containing liquid or solid particles formed by condensation of vapors produced by chemical reaction of gases or sublimation (Dennis, 1976). Generally, the particle size is in the range of 0.01 μm to 1 μm. Distinction between the terms "smokes" and "fumes" is often difficult to apply.

Mists: Suspension of liquid droplets formed by condensation of vapor or atomization; the droplet diameters exceed 10 μm and in general the pariculate concentration is not high enough to obscure visibility (Hidy and Brock, 1970).

Fogs: Same as "mists", but the particulate concentration is sufficiently high to obscure visibility (Hidy and Brock, 1970). [Dennis (1976) proposes alternate definitions that distinguish "mists" and "fogs" on the basis of particle size.]

Haze: An aerosol that impedes vision (Dennis, 1976) and may consist of a combination of water droplets, pollutants, and dust (Hidy and Brock, 1970).

Smog: A combination of "smoke" and "fog." Originally, this term referred to episodes in Great Britain that were attributed to coal burning during persistent foggy conditions (Chambers, 1976). In the United States "smog" has become associated with urban aerosol formation during periods of high oxidant concentrations.

Cloud: A free aerodisperse system of any type having a definite size and form and without regard to particle size (Fuchs, 1964).

Primary particles (or primary aerosols): Dispersion aerosols formed from particles that are emitted directly into the air and that do not change form in the atmosphere (NAS, 1977). Examples include windblown dust and ocean salt spray.

Secondary particles (or secondary aerosols): Dispersion aerosols that form in the atmosphere as a result of chemical reactions, often involving gases (NAS, 1977). A typical example is SO_4^{2-} produced by photochemical oxidation of SO_2.

In addition to classifying aerosol systems by their properties (origin, physical state, size), systems are classified according to the performance characteristics of the sampler or analyzer. Some of the more common classifications used are the following:

Aitken nuclei: Those particles and ions measured by means of an instrument in which water-vapor is made to condense on particles by supersaturating the vapor (White and Kassner, 1971). In order to eliminate condensation on light ions, the supersaturation should not exceed 270 percent (White and Kassner, 1971). The term "condensation nuclei" is often used synonymously with the term "Aitken nuclei."

Total suspended particulate (TSP) mass: The particulate mass that is collected by the high-volume sampler. (The system is classified in terms of the operational characteristics of the sampler. See the discussion in Chapter 3.)

Coarse and fine particles: These two fractions are usually defined in terms of the separation diameter of a sampler. For the dichotomous sampler (see Chapter 3), the separation diameter has usually been set at 2.5 μm. Thus, for the dichotomous sampler, the "coarse particles" are those collected by the sampler with aerodynamic diameters greater than 2.5 μm; the "fine particles" are those collected by the sampler with diameters less than 2.5 μm. (NOTE: separation diameters other than 2.5 μm have been used.)

Additional definitions that relate to particle size, particle size distributions, and particle motion will be provided in the context of the material discussed in the following sections.

2.4.2 Physical Properties of Gases and Particles

To understand the behavior of an aerosol, it is necessary to know the physical properties of the gases and particles. Such knowledge is necessary to designing particle samplers, understanding the effects of aerosols (e.g., loss of visual quality), understanding aerosol processes (such as coagulation, growth, deposition), and modeling the effects and dynamics of aerosols.

2.4.2.1 Physical Properties of Gases--An aerosol consists of two principal components: the gas-phase medium and the solid or liquid dispersed phase. The behavior of aerosol systems can be described in terms of the behavior and interaciton of these two components.

For tropospheric aerosols, the gas of interest is "air." The molecular and fluid properties of air are well established and will not be reviewed here (see Hirschfelder et al., 1954; Bird et al., 1960). The fluid motion of air, especially laminar flow, is adequately understood. Presently, turbulent flow is formulated in statistical descriptions, and often the flow fields in complex geometry cannot be satisfactorily predicted. This limitation in theory has seriously affected our ability to describe the tropospheric microscale motion of particles with diameters greater than 10 μm; specific problems include the performance of particle samplers and the formulation of particle dry deposition.

In summary:

1. The physical properties are adequately known.
2. Laminar flow of air is adequately understood.
3. Turbulent flow must be described in terms of a random fluctuating component; this limitation seriously affects our ability to describe particle motion, especially for particles with diameters greater than 10 μm.

2.4.2.2 Physical Properties of Particles--The physical properties of particles that influence behavior are divided into three types (Billings and Gussman, 1976): physical configuration, bulk material properties, and surface properties.

2.4.2.2.1 Physical configuration. The shape, structure, and density are physical configuration properties that are very important parameters in the equations of motion for particles.

The shape of particles is highly varied. Tropospheric particles have been reported to have the following types of shapes: spherical, irregular, cubical, flake, fibrous, and condensation flocs. Particle shape is related to source type, as shown in Table 2-16.

TABLE 2-16. PARTICLE SHAPES AND SOURCE TYPES[a]

Shape	Examples
Spherical	Smoke, pollen, fly ash
Irregular	Cinder
Cubical	Mineral
Flakes	Mineral, epidermis
Fibrous	Lint, plant fiber
Condensation flocs	Carbon, smoke, fume

[a] Whitby et al., 1957.

The physical dimensions of particles are usually expressed in terms of an equivalent statistical diameter. For such a measure to be meaningful for nonspherical particles, it must be applied as an average to a statistically significant number of particles (Cadle, 1975). For sizing collected particles, the most widely used "diameters" for irregular particles are:

1. Martin's diameter: The distance between opposite sides of the particle, measured crosswise of the particle, on a line that bisects the projected area and that is parallel to a reference line. (For examples, see Cadle, 1975; McCrone and Delly, 1973.)
2. Feret's diameter: The distance between two tangents on opposite sides of the particle and parallel to a reference line. (For examples, see Cadle, 1975; McCrone and Delly, 1973.)
3. The maximum horizontal intercept: The longest diameter from edge to edge of the particle, parallel to the reference line (McCrone and Delly, 1973).

4. The projected area diameter (British Standard method): Found by comparing the projected area of the particle with the areas of reference circles on an ocular graticule (McCrone and Delly, 1973).

These four "diameters" are used in powder technology. However, they are less useful for applications relating to particle dynamics. They describe the shape in terms of one or two dimensions (i.e., projected surface area). The dynamics of particle motion are formulated in terms of the diameters of three-dimensional spheres. The relation between the "diameters" measured for projected surface areas of irregular particles and the "diameter" meaningful for particle motion and light scattering is not obvious. For regular-shaped particles (e.g., cubes, cylinders, oblates), Fuchs (1964) has derived dynamic shape factors that permit their representation as equivalent spheres.

The density (mass per unit volume) of particles is important because it affects motion and behavior. The density of particles that are spheres, cubes, and other regular geometries is the same as the density of the bulk material. However, many particles are agglomerates of smaller particles of various composition. A large percentage of the volume of such agglomerates is voids or air-filled pores. Such a structure has the appearance of a cluster of grapes. The sum of the volume of the small solid/liquid particles plus the void volume is defined as the "apparent" volume of the agglomerate. The "apparent density" of agglomerates is defined as the ratio of solid/liquid mass to the apparent volume (Fuchs, 1964), and it is often 2-10 times lower than the density of mass that excludes the pore volume (Hesketh, 1977).

Because many tropospheric particles are irregular or agglomerates and have unknown density, it is common practice to represent the shape, structure, and density of particles in terms of dynamically equivalent spheres of unit density. Hence, the following definition: Aerodynamic diameter: The diameter of a sphere of unit density (1 g/cm^3) that attains the same terminal velocity at low Reynolds number in still air as the actual particle under consideration.

2.4.2.2.2 Bulk material properties. The bulk material properties that affect aerosol behavior include chemical composition, vapor pressure, hygroscopicity and deliquescence, and index of refraction. These properties are of interest because they control (a) the physical state and growth, and (b) the scattering and absorption of light by tropospheric particles.

The chemical composition of tropospheric particles will be discussed briefly in Section 2.4.5 and in more detail in Chapter 5. It is sufficient to point out here that the particles with diameters less than approximately 2.5 μm contain most of the SO_4^{2-}, H^+, and NH_4^+ and a significant fraction of the NO_3^- and Cl^-; therefore, these particles interact with H_2O vapor much more strongly than larger particles (Meszaros, 1971; Charlson et al., 1978).

The most important systems are those of H_2SO_4, NH_4HSO_4, and $(NH_4)_2SO_4$. The most important aqueous systems are those containing H^+, NH_4^+, SO_4^{2-}, NO_3^-, and Cl^- since these species are usually present in sufficient mass to control the liquid water concentration and the phase transition points of particles as a function of relative humidity. Presently, phase diagrams for this multicomponent system are not available for conditions relevant for tropospheric particles. However, the phase diagram for the H^+-NH_4^+-SO_4^{2-}-H_2O system at equilibrium is shown in Figure 2-7. On this diagram, the dry, pure crystals $(NH_4)_2SO_4$, $(NH_4)_3(HSO_4)_2$, and $(NH_4)HSO_4$ are indicated as points A, B, and C, respectively. If letovicite, $(NH_4)_3H(SO_4)_2$, is exposed to relative humidities that start at 0 and increase to 100 percent, its behavior can be described in terms of the locus BO in Figure 2-7. From 0 percent r.h., the salt immediately enters the 3-phase zone consisting of $(NH_4)_3H(SO_4)_2$, $(NH_4)_2SO_4$, and some liquid solution of H^+, NH_4^+, and SO_4^{2-}. At point D, the locus intersects a phase boundary for $(NH_4)_3H(SO_4)_2$ and a partial deliquescence occurs. Between the point D and the intersection with curve EE_1, solid $(NH_4)_2SO_4$ remains; however, at the intersection of EE_1, a second and complete deliquescence occurs. From EE_1 to point 0, only the solution phase is present. In similar fashion, equilibrium trajectories for salts subjected to varying composition and relative humidity can be traced. The locus EE_2 demonstrates the dependence of the complete deliquescence point r.h. on the weight percent H_2SO_4; as the system's acid composition changes from 0 to 35 percent, the complete deliquescence point r.h. changes from 80 to 39 percent. Thus, it is obvious that NH_3 plays a key role in governing the phase transition points.

The H_2SO_4, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, and $(NH_4)_2SO_4$ particle systems have been characterized recently by Charlson et al. (1978), Tang et al. (1976), Tang and Munkelwitz (1977), and Tang (1980a). Charlson et al. (1978), used an apparatus in their studies that measured the light scattering coefficient of the aerosol as a function of the relative humidity. They obtained good agreement between theory and experiment in observing the hygroscopic behavior of H_2SO_4. However, they observed no deliquescence point for NH_4HSO_4 particles, and one at ~38 percent r.h. for $(NH_4)_3H(SO_4)_2$ particles. The bulk salts have a deliquescence point at 39 percent and 69 percent r.h., respectively. They suggested that the deliquescence point for NH_4HSO_4 particles may not have been exhibited because the initial droplets which were only dried to 15 percent r.h. entered a hysteresis loop, forming supersaturated solution droplets. Their observation of a growth point for $(NH_4)_3H(SO_4)_2$ particles at ~38 percent r.h. but not the deliquescence point at 68 percent r.h. is difficult to explain, but it may have been due also to the particles forming supersaturated droplets and entering a hysteresis loop. If that were the case, then the true deliquescence point at 69 percent r.h. would not be exhibited, and the observed transition at ~38 percent may be an efflorescence point. Efflorescence points of solution droplets exposed to decreasing relative humidity are not sharp and usually occur at relative humidities more than 30 percent below the deliquescence point. Tang (1980a) used a system in which the salt aerosol was first dried, and then passed through a controlled humidity chamber; the particles were sized with a single-particle optical analyzer. His data on deliquescence points and hygroscopic growth agreed well with theory, as is shown in Figure 2-8, and he concluded that for the NH_4HSO_4-H_2O systems that the equilibrium size of mixed-salt droplets may be adequately predicted from bulk solution properties. (The Kelvin effect, which

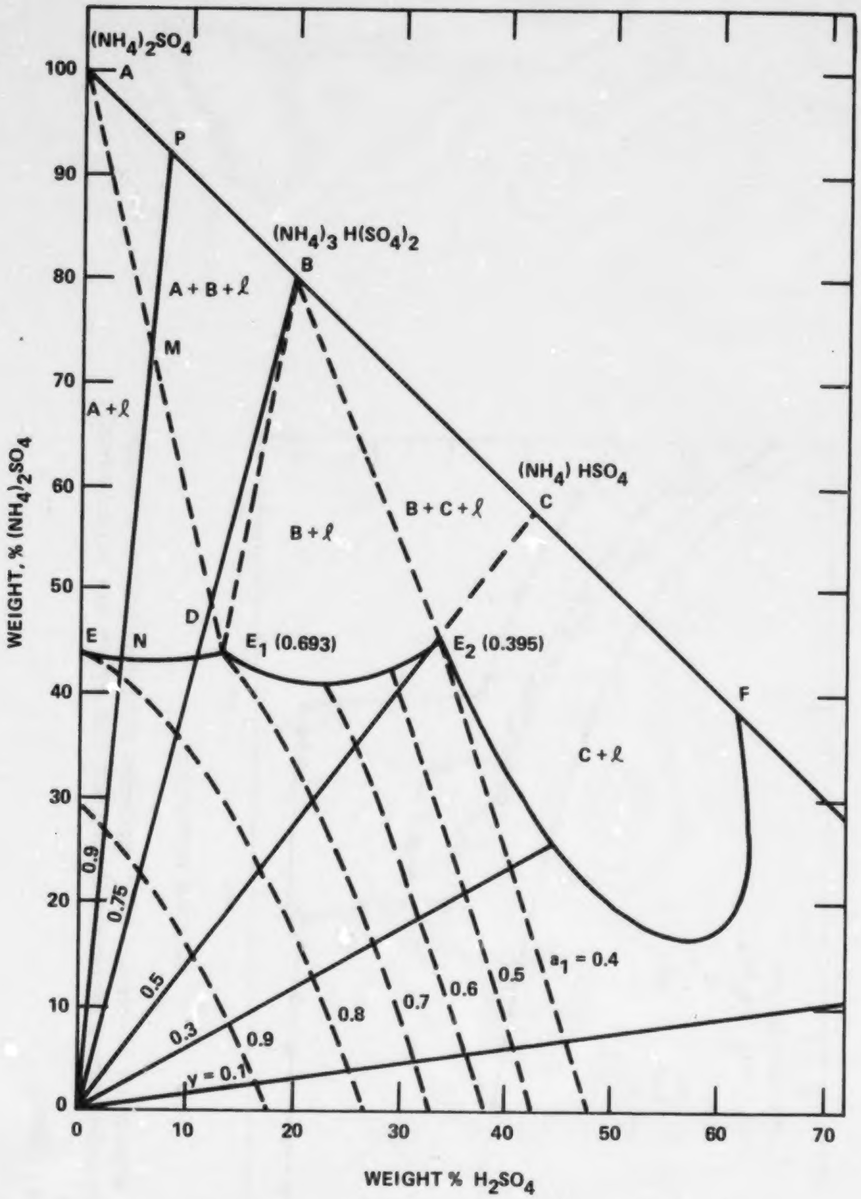

Figure 2-7. Solubility diagram for the $H^+-NH_4^+-SO_4^{2-}-H_2O$ system at equilibrium (30°C).

A = solid phase of $(NH_4)_2SO_4$
B = solid phase of $(NH_4)_3H(SO_4)_2$
C = solid phase of $(NH_4)HSO_4$
= liquid solution phase
a_1 = activity of water
= fractional relative humidity
y = mole fraction of $(NH_4)_2SO_4$

The numbers in parentheses are the fractional relative humidities for the complete deliquescence points that are indicated.

Source: Tang (1980a).

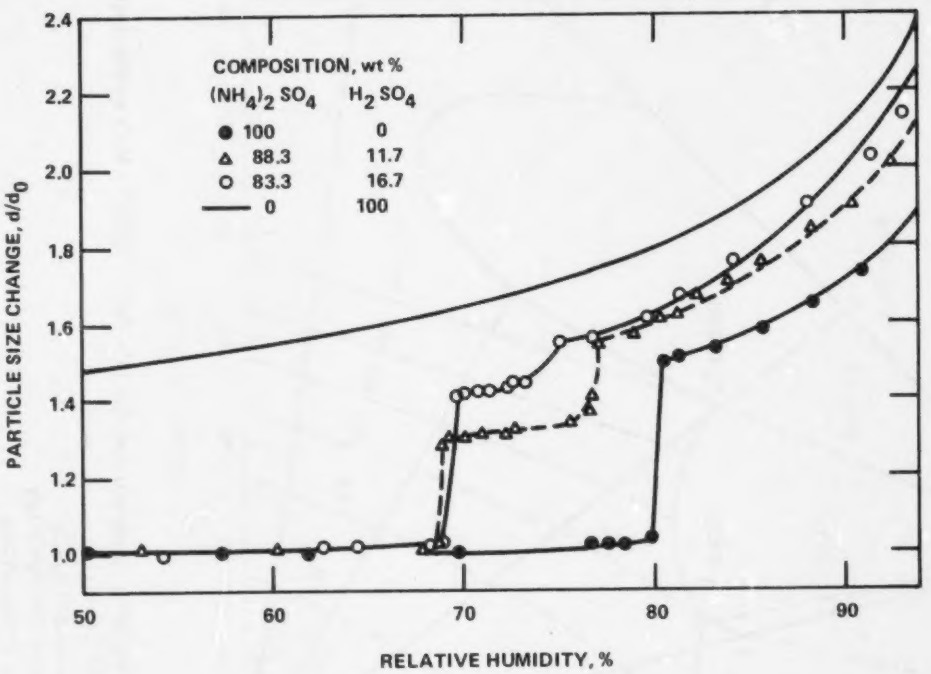

Figure 2-8. Growth of $H^+-NH_4^+-SO_4^{2-}$ particles as a function of a relative humidity. The solid curves represent theory and the points are experimental observations.
Source: Tang (1980a).

may limit growth, is discussed in Section 2.4.4.) Tang (1980a) also demonstrated the hysteresis phenomenon for $(NH_4)_2SO_4$ particles; it can be seen in Figure 2-9 that as the particles were subjected to decreasing relative humidity, solid crystals did not form at the deliquescence point (79.5 percent r.h.), but formed at about 30 percent r.h. (in agreement with the observations of Orr et al., 1958).

The deliquescence and efflorescence points of salt particles relevant to environmental investigations are presented in Table 2-17.

TABLE 2-17. DELIQUESCENCE AND EFFLORESCENCE POINTS OF SALT PARTICLES[a]

Composition	Deliquescence, % r.h.	Efflorescence, % r.h.
NaCl	75.7	43
KCl	84.3	53
NaCl-KCl	73.8	38
$(NH_4)_2SO_4$	79.5	~36
$(NH_4)_3H(SO_4)_2$	69.0	
NH_4HSO_4	39.0	
$2NH_4NO_3 \cdot (NH_4)_2SO_4$	56.4	

[a] Adapted from Tang (1980a).

It will be pointed out in Section 2.4.5.2 and in Chapter 5 that the composition of tropospheric particles may consist of many species. In general, it is not known if the individual particle is essentially a pure compound in a population of particles of various compounds (external mixture) or if the individual particle contains a mixture of compounds (internal mixture) (Winkler, 1975). The composition of the individual particles governs their size as a function of the relative humidity. For two-component droplets smaller than 0.05 μm, the surface curvature affects the vapor pressure of the droplets, and their size is related to the relative humidity through the modified Kelvin-Gibbs equation (Nair and Vohra, 1975):

$$\ln(p/p_o) \doteq \ln a_w = \frac{2M\sigma}{RT\rho r}\left[1 + \frac{x}{\rho}\frac{d\rho}{dx} - \frac{3x}{2\sigma}\frac{d\sigma}{dx}\right] \qquad (2\text{-}47)$$

where p = vapor pressure over the curved surface
p_o = vapor pressure over a flat surface
σ = surface tension
M = molecular weight of water vapor
ρ = density
x = solute mass fraction

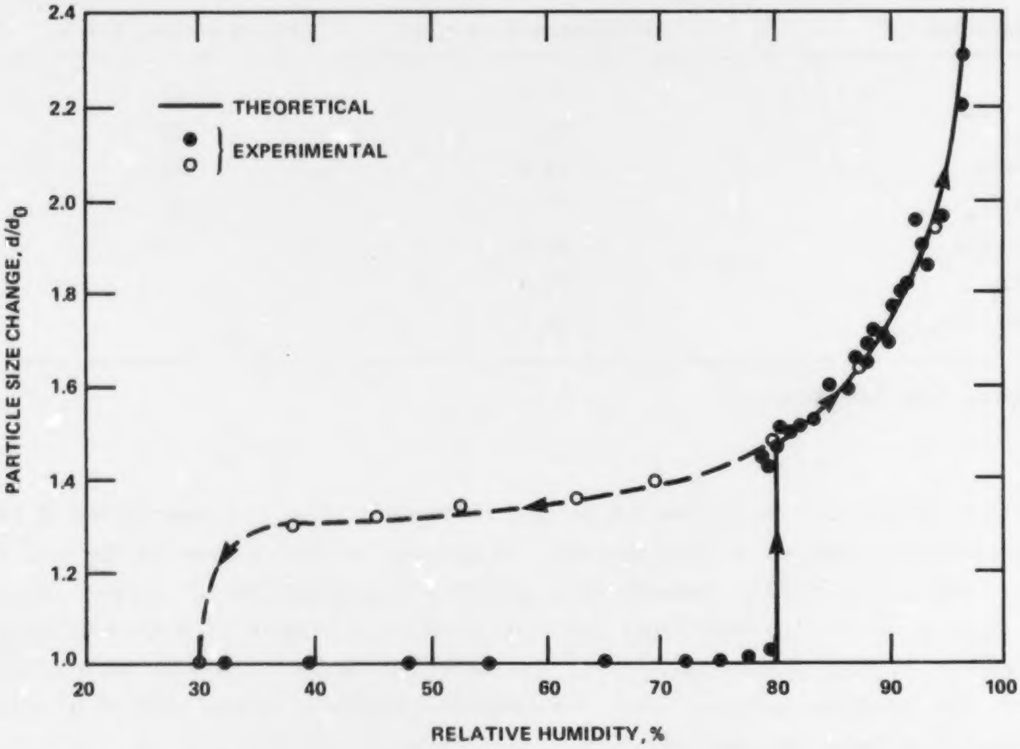

Figure 2-9. Condensational growth and evaporation of $(NH_4)_2SO_4$ particles as a function of relative humidity at 25°C.

Source: Tang (1980a).

R = universal gas constant

T = temperature

r = radius

a_w = activity of water

Nair and Vohra (1975) added the terms in the square brackets on the right side of Equation 2-47 to correct the Kelvin-Gibbs equation for the variation of surface tension and density as a function of concentration. The behavior of particles that are external and internal mixtures can be described by Equation 2-47. However, the Nair and Vohra (1975) modification has been recently challenged (Renninger et al., 1981) on the basis that nucleation theory may have been used incorrectly to derive the thermodynamic expression Equation 2-47. Presently, the issue has not been resolved (Doyle, 1981) and the validity of Equation 2-47 is not known. In general, the activity of water (a_w) is known only for pure salt solutions, with notable exceptions, such as ocean water, which makes the equation (if correct) immediately applicable only to external mixtures. There have been attempts (Fitzgerald, 1975; Hänel and Zankl, 1979; Sangster and Lenzi, 1974) to calculate a_w for multicomponent electrolyte solutions without resorting to detailed theory. Hänel and Zankl (1979) compared the results for two mixture rules: (a) the mass of water condensed on the mixed electrolyte is equal to the sum of the masses of water condensed on the separated pure components, and (b) the practical osmotic coefficient is equal to the molality-weighted practical osmotic coefficient of the separated pure components. The first mixture rule gave the better acuracy, but to limit errors to 10-15 percent, Hänel and Zankl advised that it be used only for water activities larger than 0.85 to 0.9, which corresponds to relative humidities of 85 to 90 percent. Thus, for known internal mixtures, the change in droplet size as a function of relative humidity can be calculated adequately only for high humidities (greater than 85 to 90 percent).

Ideally, the growth behavior (especially at deliquescence points) of particles as a function of relative humidity offers a means of distinguishing internal/external mixtures and of identifying the predominant salts. However, both the likelihood that atmospheric particles also exhibit hysteresis by forming supersaturated salt solutions and our inability to predict accurately the activity of water for multicomponent mixtures for relative humidities below about 85-90 percent militate against this approach.

The growth of H_2SO_4 droplets with dry mass in the range of 10^{-19} to 10^{-12}g and their concentrations (normality) are shown in Figure 2-10, which is based on Equation 2-47 and the data given in Table 2-18 (Nair and Vohra, 1975). However, as previously pointed out in this section, the validity of Equation 2-47 has been questioned; thus, the information in Figure 2-10 must also be questioned until the issue of the validity of Nair and Vohra's (1975) modification is resolved. As Figure 2-10 shows, in the absence of atmospheric NH_3, H_2SO_4 droplets are highly acidic. For example, at relative humidities $\leq$40 percent, the concentration of H_2SO_4

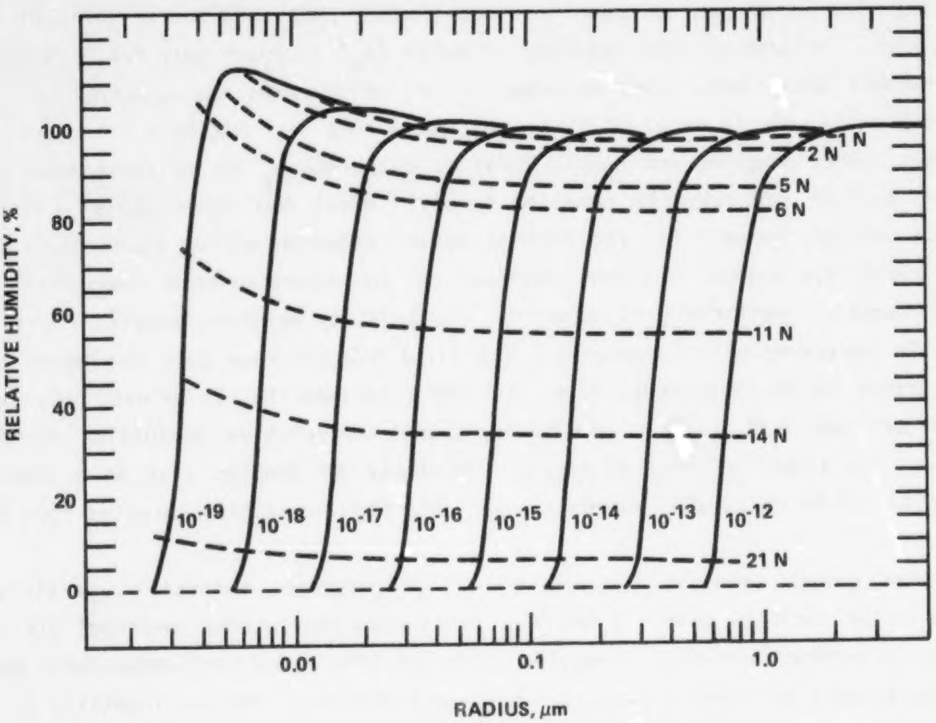

Figure 2-10. The equilibrium size of sulfuric acid solution droplets as a function of relative humidity. The mass of sulfuric acid (from 10^{-19} to 10^{-12} gram) is indicated on the growth curves (solid). The normality (N) of the solution is marked for selected values from 1 N to 21 N (dashed lines).

TABLE 2-18. SULFURIC ACID SOLUTION VALUES (25°C)

H_2SO_4 Mass % x	ρ g cm^{-3}	$d\rho/dx$ $\times 10^3$	σ dyn cm^{-1}	$d\sigma/dx$ $\times 10^2$	a_w	H_2O/H_2SO_4 mole ratio	Normality
0.5	1.000	8.1	72.0	12.0	0.998	1081.0	0.102
1.0	1.004	7.4	72.1	8.6	0.996	537.8	0.206
5.0	1.030	6.7	72.3	5.5	0.982	103.2	1.03
10.0	1.064	7.0	72.6	8.0	0.958	48.9	2.18
20.0	1.136	7.5	73.7	11.4	0.880	21.7	4.65
25.0	1.175	7.9	74.3	11.3	0.823	16.3	6.00
40.0	1.299	8.8	75.8	10.0	0.555	8.1	10.7
50.0	1.391	9.8	76.8	6.4	0.340	5.4	14.2
66.0	1.560	11.3	75.2	-30.0	0.075	2.8	21.0
85.0	1.773	8.7	68.7	-72.0	0.001	1.0	30.6

Source: Adapted from Nair and Vohra (1975) is $\geq 14\underline{N}$. Increases in the relative humidity up to 100 percent cause great reductions in H_2SO_4 concentrations for droplets with dry mass $>10^{-16}$g. At 100 percent r.h., these droplets grow without bounds and become infinitely dilute. However, droplets with H_2SO_4 dry mass $<10^{-16}$g have their growth restricted by the Kelvin-Gibbs effect, which is expressed in the right-hand side of Equation 2-47. Such droplets have a critical radius at relative humidity >100 percent that prevents unbounded growth. As an example, the droplet with dry mass of 10^{-19}g H_2SO_4 attains a radius of 0.004 µm and concentraiton of $6\underline{N}$ at 100 percent r.h.; it has a critical radius of ~0.005 µm which can be attained at ~114 percent r.h. As long as the relative humidity does not exceed 114 percent, the droplet's size is governed by the portion of the curve to the left of the critical radius (0.005 µm); if the relative humidity becomes ≥114 percent, and the critical radius is reached, the droplet will then grow without bounds as long as the relative humidity is ≥100 percent. For ambient air and breathing, the relative humidity does not exceed percent. Thus, from Figure 2-10, it is easy to see that small H_2SO_4 droplets (with dry mass $<10^{-16}$g) might pose serious threats to health, as hypothesized by Stauffer (1974). If inhaled, such droplets would attain H_2SO_4 concentrations of 2 to $6\underline{N}$ for dry masses of 10^{-16} to 10^{-19}g, respectively, if not neutralized by NH_3.

Cl^- and NO_3^- may be displaced as HCl and HNO_3 from solution droplets or thin aqueous films on particles by H_2SO_4. Although the order of the relative acid strengths is HCl > H_2SO_4 > HNO_3 (see Table 2-4), their vapor pressures do not have the same order. The acid-gas vapor-pressures over aqueous solutions are given by:

$$\begin{aligned} P_{HCl} &= (\underline{H}_{HCl})(a_{HCl}) = (\underline{H}_{HCl})(K_{HCl})^{-1}(a_{H^+})(a_{Cl^-}) \\ &\cong 5 \times 10^{-6} \text{ atm } M^{-2} (a_{H^+})(a_{Cl^-}) \end{aligned} \tag{2-48}$$

$$\begin{aligned} P_{HNO_3} &= (\underline{H}_{HNO_3})(a_{HNO_3}) = (\underline{H}_{HNO_3})(K_{HNO_3})^{-1}(a_{H^+})(a_{NO_3^-}) \\ &\cong 2 \times 10^{-7} \text{ atm } M^{-2} (a_{H^+})(a_{NO_3^-}) \end{aligned} \tag{2-49}$$

$$\begin{aligned} P_{H_2SO_4} &= (\underline{H}_{H_2SO_4})(a_{H_2SO_4}) = (\underline{H}_{H_2SO_4})(K_{1,H_2SO_4})^{-1}(a_{H^+})(a_{HSO_4^-}) \\ &\cong 3 \times 10^{-11} \text{ atm } M^{-2} (a_{H^+})(a_{H^+})(a_{SO_4^{2-}}) \end{aligned} \tag{2-50}$$

The Henry's Law constant $\underline{H}_{HCl}$($\cong$ atm M^{-1}) was calculated from the free energy change for $HCl_{(aq)} \rightleftarrows HCl_{(g)}$ (Cotton and Wilkinson, 1980). The value of $\underline{H}_{HNO}$ (= 4.8 x 10^{-6} atm M^{-1}) has been reported by Schwartz and White (1981). Only recently has $H_2SO_{4(g)}$ vapor pressure become available for aqueous solutions (Roedel, 1979; Chu and Morrison, 1980). The value of $\underline{H}_{H_2SO_4}$ (=3 x 10^{-8} atm M^{-1}) was estimated from Roedel's (1979) data for 82 percent (mass) H_2SO_4. Thus, from these vapor pressure equations it can be seen that the vapor pressure of $H_2SO_{4(g)}$ will be orders of magnitude less than $HNO_{3(g)}$ and $HCl_{(g)}$ for tropospheric particles. In acidic solutions, H_2SO_4 is effective in volatilizing HNO_3 and HCl, causing these acids either to reside in the gas phase or to recondense on less acidic particles (Harker et al., 1977; Hitchcock et al., 1980).

The influence of NO_3^- is an important consideration. Tang (1980b) has performed detailed qualitative calculations of the partial pressures of NH_3 and HNO_3 over the NH_3-HNO_3-H_2SO_4-H_2O system at 25°C. His calculations for the partial pressures P_{NH3} and P_{HNO3} over this system at 85 percent relative humidity are shown in Figure 2-11. The solution composition ranges from pure H_2SO_4 ($[NH_4^+]/[SO_4^{2-}] = 0$) to pure $(NH_4)_2SO_4$ ($[NH_4^+]/[SO_4^{2-}] = 2$). The P_{HNO3} has almost a linear dependence on $[NH_4^+]/[SO_4^{2-}]$, while P_{NH3} is not sensitive to this parameter, but depends only on solution pH. Figure 2-11 demonstrates the complex interactions among NH_3, HNO_3, and H_2SO_4. He also studied the effects of relative humidity and pH on these partial pressures and deduced that: (1) the HNO_3 partial pressure depends strongly on both the relative humidity and droplet pH, and (2) the NH_3 partial pressure varies only slightly with humidity but inversely with H^+ concentration. Tang (1980b) remarked that the strong dependence of the HNO_3 partial pressure on relative humidity may affect the nitrate content of particles that are sampled, leading to biases in the determination of ambient NO_3^-.

Charlson et al. (1978) have reviewed the potential use of the difference in the indices of refraction for differentiating ambient particles of H_2SO_4 and $(NH_4)_2SO_4$. The ratio of backward hemispheric scattering to the total scattering was measured near St. Louis in 1973 during periods that were classified as H_2SO_4 or $(NH_4)_2SO_4$ dominated events. While the observed differences were generally in the right direction, the average value of the backward/total scatter ratio did not agree with prediction, which led Charlson et al. (1978) to conclude that refractive index is too complex a variable to be used as an analytical tool for differentiating the types of SO_4^{2-} systems.

In summary:

1. Bulk material properties are adequate in most cases for describing the state of tropospheric particles.
2. However, there is a paucity of thermodynamic data to permit prediction of deliquescence and hygroscopic behavior and vapor pressures of multicomponent systems, especially for relative humidities below about 90 percent.

2.4.2.2.3 Surface properties. The surface properties of particles provide means of detection, measurement, and collection; and may increase persistence of droplets in the atmosphere. Some of the more important surface properties are: electrostatic charging, adhesion, and the influence of surface films.

A number of identifiable mechanisms can lead to electrostatic charging of particles including contact charging, photoionization, field emission charging, and gaseous ion capture. For practical applications in the troposphere, gaseous ion capture is the most important of these mechanisms. Contact also produces charging, as in the triboelectric charging of dust

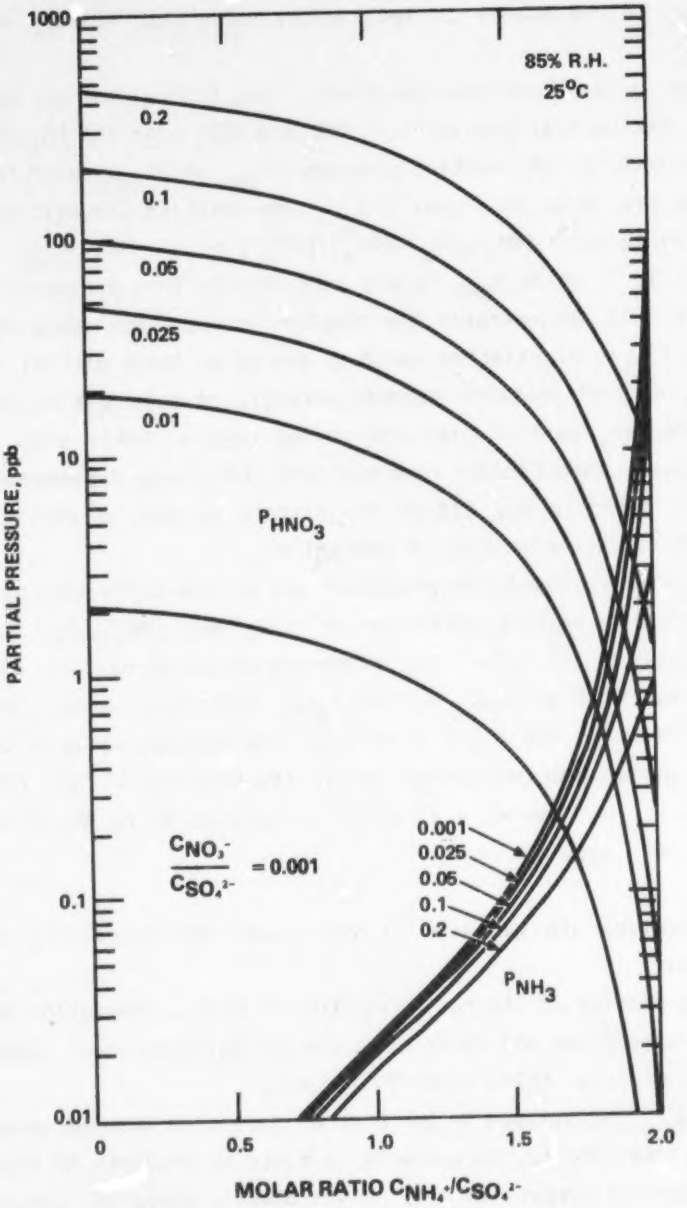

Figure 2-11. NH_3 and HNO_3 partial pressures as a function of droplet's nitrate ($C_{NO_3^-}$) and sulfate ($C_{SO_4^{2-}}$) concentrations at 85% relative humidity, 25°C.

Source: Tang (1980b).

blown by wind along the earth's surface. Bursting bubbles may produce charged sea spray aerosols over the ocean.

Reviews of experiment and theory for gaseous ion capture by aerosol particles may be found in papers by Bricard (1977) and by Whitby and Liu (1966). Two recognized capture mechanisms are field charging and diffusion charging. Field charging denotes the process in which an ion is captured by a particle through the influence of an external electrical field. Diffusion charging is a process in the absence of an external electrical field. Field charging of aerosol particles is used in particle control technology for the operation of electrostatic precipitators. Diffusion charging is employed in classification or sizing of aerosol particles according to their electrical mobility.

The rate of gaseous ion capture by an aerosol particle depends upon a number of parameters including the particle size and shape, the dielectric constant of the particle, the number of charges already on the particle, and the mean free path and mobility of the gaseous ion, plus, for field charging, the external electrical field strength.

The charging of an aerosol has been shown by Boisdron and Brock (1970) to be a stochastic process. Inherent difficulties in the use of particle charging as an aerosol detection method have been shown by Marlow (1978a and 1978b) and by Porstendorfer and Mercer (1978). These studies indicate that the polydispersity of the aerosol, the dielectric constant of the particles, and humidity in the presence of trace gases lead to uncertainties in aerosol particle charges.

Particles are removed from the troposphere by diffusion to or impaction against surfaces. Particles also collide with each other and stick together. The forces of adhesion that hold particles to surfaces and to each other include electrostatic forces, capillary forces in the presence of a liquid, and London-van der Waals forces. In general, for uniform conditions, the efficiency of particle removal from surfaces by air flow decreases as the particle size decreases for dry, solid particles (Corn, 1976). While the types of forces are known, the magnitude of these forces usually cannot be predicted precisely.

The influence of surface films on aqueous droplets has been recognized for many years (Bradley, 1955; Eisner et al., 1960). Chang and Hill (1980) have reviewed some of the studies on droplet stabilization by surface films. They have also demonstrated that the products of the reaction between O_3 and 1-decene in humid air contain species that adsorb on water droplets and retard the evaporation rate. Chang and Hill (1980) suggest that photochemical reactions may produce similar products that would retard the evaporation of urban fogs, and perhaps extend their duration by hours. However, they report no kinetic data. Eisner et al. (1960) investigated the kinetics of evaporation of droplets with fatty alcohols on the surface. They were able to increase the lifetime of an evaporating 10-μm droplet only by a factor of about 250, which corresponds to about 2.5 minutes. (Another likely cause of stable fogs is the formation of supersaturated droplets.) At this time, the influence of photochemically produced organic condensates on the kinetics of droplet evaporation is not known.

2.4.3 Dynamics of Single Particles

The behavior af atmospheric aerosols depends upon the physical properties of the suspending gas, the particles, gas-particle interactions, particle-particle interactions, and the fluid motion of the gas. Knowledge of these properties and interactions is essential to our understanding of atmospheric phenomena, our ability to formulate predictive models of pollutant particle concentrations and effects, and our ability to sample and measure particles. In this section, the conditions will be presented for which aerosol systems can be described in terms of the dynamics of single particles.

According to Hidy and Brock (1970), particles may be considered to be independent of each other and the dynamics of single particles may be applied if the conditions in Table 2-19 are satisfied. If coagulation or deposition are important processes, and the stystem satisfies all but the last condition, they refer to the system as being in the "quasi-single particle regime." As is seen in Table 2-19, the conditions for the "single particle regime" are generally satisfied for the troposphere.

TABLE 2-19. CONDITIONS FOR THE SINGLE-PARTICLE REGIME[a]

Conditions[b]			Range in Troposphere
1. n_i/n_G	<< 1	for all i	$\sim 10^{-13}$ to 10^{-19}
2. $\lambda_G n_i^{1/3}$	<< 1	for all i	$\sim 10^{-3}$ to 10^{-5}
3. $R_i n_j^{1/3}$	<< 1	for all i,j	$\sim 10^{-1}$ to 10^{-7}
4. $n_i^{1/3} L_{vi}$	<< 1	for all i	~ 0
5. $Q_i Q_j \kappa/kT$	<< 1	for all i,j	$\sim 10^{-2}$ to 10^{-6}

[a] From Hidy and Brock (1970).

[b] n_i = number concentration of particles of type i

n_G = number concentration of air molecules ($\sim 10^{19} cm^{-3}$)

λ_G = mean free path of air molecules ($\sim 10^{-5}$ cm)

R_i = radius of particle, cm

L_{vi} = characteristic distance (cm) associated with change in number concentration, temperature, and velocities

Q_i = electrostatis charge, esu

κ = Debye reciprocal length (effective distance of Coulombic interaction), cm^{-1}

k = Boltzmann' constant (= 1.38×10^{-16} erg/K-mole)

T = temperature, K

The dynamics of single particles include sedimentation, impaction, diffusion, coagulation, electrodynamics, and filtration (Fuchs, 1964; Hidy and Brock, 1970; Friedlander, 1977). In general, the dynamics can be described adequately for all particle sizes in calm air. According to Fuchs (1964), complete (~99 percent) entrainment of particles by eddy fluctuations occurs if

$$\tau/t_L < 0.02 \tag{2-51}$$

where

τ = particle relaxation time

= $\frac{V_o V_s}{g}$

V_o = initial velocity of particle in the absence of external forces, cm/sec

V_s = terminal (steady) settling velocity of particle in still air, cm/sec

g = gravitational constant

t_L = the Lagrangian period of eddy fluctuations, sec

= $0.5\pi\lambda/\upsilon_\lambda$

λ = scale length of eddy fluctuations, cm

υ_λ = root mean square (rms) eddy velocity corresponding to fluctuations on a scale $\leq \lambda$, cm/sec.

Using an rms eddy velocity of 30 cm/sec, which is a typical value ~1 m above the ground, and $\lambda \simeq 40$ cm at $\lambda/\upsilon_\lambda \simeq 1$; in this case, $\tau/t_L \simeq 0.01$ for a particle (unit density) with a diameter of 10 μm. That means particles with diameter < 10 μm will be >99 percent density entrained in the atmospheric eddy fluctuations. As the rms eddy velocity increases above 30 cm/sec and the particle approaches nearer to the surface or a large obstacle, t_L decreases, τ remains constant, and thus the particle diameter corresponding to ~99 percent entrainment must decrease from 10 μm. It is important to note that larger particles with diameters >1 mm have $\leq$ 2 percent entrainment in the eddy fluctuations for these conditions (Fuchs, 1964), which is adequate justification for ignoring the influence of atmospheric turbulence on their motion. Thus, the following practical limits for considering atmospheric motion can be stated:

a. Diameter $\leq$10 μm: The particles follow the eddy motion with 99 percent entrainment

b. 10 μm < diameter < 1 mm: The particles lag behind the eddy motion

c. Diameter > 1 mm: The particles do not follow the eddy motion.

These practical limits suggest that in turbulent atmospheres the dynamic behavior of particles with diameter <10 μm can be described in terms of viscous flow mechanics with superimposed eddy flow. The dynamic behavior of particles with diameters in the range 10 μm to 1 mm cannot be similarly described (see Soo, 1967; Fuchs, 1964), and satisfactory approaches are still fertile areas for research. The inability to describe completely the motion of such particles in turbulent air has had an inhibiting effect on the design and use of aspiration samplers for particles with diameter >10 μm (May et al., 1976). A practical method to reduce biases in aspirating samplers caused by the inertial effects of flowing large particles is to sample isokinetically, which means that the air streamlines neither converge nor diverge upon entering the sampler. Isokinetic sampling is attempted by matching the inlet flow velocity of the sampler to the local air flow velocity. However, even under ideal conditions, the probe extends a disturbance upwind of the inlet, causing entrance biases for particles having appreciable inertia (Fuchs, 1964). In the turbulent atmosphere, it is not practical to attempt isokinetic sampling which would require: (a) a fast-response realigning inlet that can maintain its axis parallel to the local, rapidly fluctuating wind vector, (b) a fast-response pumping system that can maintain the inlet flow speed equal to that of the wind's, and (c) a thin-walled inlet (Belyaev and Levin, 1974). The most common atmospheric particle samplers (e.g., high volume samplers, dichotomous samplers; see Chapter 3) are operated anisokinetically. For real, fluctuating turbulent atmospheres, actual trajectories for unit density particles greater than ~10 μm diameter cannot be calculated; instead, the trajectories are estimated by ignoring turbulence. While turbulent wind tunnel tests of sampler inlet efficiencies can be performed under steady conditions (Wedding and Weigand, 1980; Liu and Pui, 1981; McFarland et al., 1977), the turbulence in the wind tunnels in general is much lower than atmospheric levels. The degree of correspondence between wind-tunnel characterizations and performance of aspirating inlets in turbulent atmospheres is not known; however, for particles in the low portion (10-15 μm) of the nonviscous flow range, significant differences in the inlet's entrance efficiency are unlikely. For particles in the complete nonviscous range (10 μm - 1 mm), no practical inlet has been demonstrated at atmospheric turbulent conditions. To date, it appears that the only reliable atmospheric particle size data for diameter >10 μm has been obtained with Rotorod and similar samplers that draw the impactor stages through the air instead of aspirating air through a fractionating device (May et al., 1976; Noll and Pilat, 1971; Johnson, 1976).

The influence of the variety of elevations and temperatures in the United States on particle formation, growth, and motion must be considered. The important mass transport parameters for air that influence particle dynamics and that change with altitude and temperature are atmospheric pressure (or density) and air viscosity. Typical values for several elevations and temperatures are shown in Table 2-20.

As shown in Table 2-20, viscosity is independent of altitude over the range considered. Within the contiguous 48 States, the acceleration due to gravity (g) varies within the range of 9.790 to 9.809 m/sec^2; this variation is so small that it will have significant effects only on precise fundamental investigations. The general shift in particle behavior as a function of air temperature, pressure, and viscosity is given in Table 2-21. The dependence of particle mechanics on these variables is well known; for many instruments and samplers that use particle mechanics for sizing and separating, the effects of changes in temperature, pressure, and viscosity must be considered.

2.4.4 Formation and Growth of Particles

Particles are formed by two processes: (1) grinding or atomization of matter, and (2) nucleation of supersaturated vapors. The particles formed in the first process may be emitted

TABLE 2-20. MASS TRANSPORT PARAMETERS FOR AIR

Elevation, km	Standard Pressure[a] kPa	Density[b], kg m^{-3}		Molecular Mean-Free Path[b], nm		Viscosity[c], kg $m^{-1}sec^{-1}$	
		-30°C	20°C	-30°C	20°C	-30°C	20°C
0	10.33 (1.00 atm)	1.56	1.29	54.0	65.3	1.54	1.81
1.52 (5,000 ft)	8.56 (0.83 atm)	1.30	1.07	64.8	78.8	1.54	1.81
3.05 (10,000 ft)	7.07 (0.68 atm)	1.06	0.88	79.2	95.4	1.54	1.81

[a] Fairbridge (1967)

[b] Weast (1976)

[c] Bretsznajder (1971)

NOTE: -30°C = -22°F; 20°C = 68°F.

directly into the atmosphere. However, the particles formed in the second process usually result from reactions of gases in the atmosphere to yield compounds with low vapor pressures; when such species reach sufficiently high supersaturation, they nucleate to form particles. The dynamics of nucleation, which are still understood only incompletely, have been extensively reviewed by Hidy and Brock (1970), who discuss the two types described below:

1. Homogeneous nucleation is the formation of particles by the molecular agglomeration of supersaturated vapors in the absence of foreign particles and ions. Important examples include the formation of particles by H_2SO_4 molecules produced by the reaction of HO radical with SO_2, and carboxylic acids formed by the reaction of O_3 and olefins.
2. Heterogeneous nucleation is the condensation of molecules of a supersaturated vapor onto foreign particles or ions. Important examples include the condensation of hydrocarbon vapors onto Pb halide and carbon particles during cooling of automobile exhaust, and the condensation of H_2SO_4 molecules onto fly ash during the cooling of plumes form power plants burning fossil fuels. Heterogeneous nucleation occurs when foreign nuclei are plentiful and may suppress the critical supersaturation pressure below the critical value required for homogeneous nucleation.

Particle growth in the atmosphere occurs through gas-particle interactions, which will be discussed in this section, and particle-particle interactions (coagulation), which are well understood and mentioned above in Section 2.4.3.

TABLE 2-21. DEPENDENCE OF PARTICLE BEHAVIOR ON AIR TEMPERATURE, PRESSURE, AND VISCOSITY

Behavior	Dependence for variation within the ranges given in Table 2-17		
	Temperature, T	Pressure, p	Viscosity, η
Nucleation rate[a]	increases in complex fashion as T increases	probably none	none
Condensation growth rate[a]			
a. Nonvolatile species	increases as a function of $T^{1.5}$	depends on p^{-1}	none
b. Volatile species	complex; may decrease due to increase in partial vapor pressure of volatile species	depends on p^{-1}	none
Sedimentation velocity in calm air[b]	dependence appears through η; as T increases, η increases	none for viscous flow; slight decrease for nonviscous flow (i.e., diameter = 100 μm) as p increases	depends on η^{-1}
Impaction parameter and stop distance[b]	none	none for viscous flow	depends on η^{-1}
Diffusion coefficient[b]	increases in a complex fashion as T increases	decreases in a complex fashion as p increases	depends on η^{-1}
Electrical mobility[b]	dependence appears through η; as T increases, η increases	increases in complex fashion as p increases	depends on η^{-1}

[a] See Hidy and Brock (1970) for general discussion.

[b] See Fuchs (1964) for equations with dependence on T, p (or mean free path length), and η.

Gas-particle interactions include the absorption and the adsorption of pollutant gases, such as SO_2, NO_2, hydrocarbons, O_3, and H_2O_2, followed by their chemical reactions to yield products such as SO_4^{2-}, NO_3^-, and organic compounds. Also included is the condensation of low vapor-pressure molecules formed in gas-phase reactions, such as H_2SO_4 and organic compounds. An important limitation on the accumulation of chemical species on submicrometer particles is the Kelvin-Gibbs effect. The vapor pressures of the solvent and solute (or surface-absorbed species) are increased as surface curvature is increased. For a condensing species being formed by gas-phase reactions, there will be a minimum particle size below which condensation will not occur; this value is determined in part by the supersaturation reached by the species (Friedlander, 1977).

2.4.4.1 Growth Dynamics--Knowledge of the mass transfer process is necessary to understanding the growth of particles due to gas-particle reactions in the troposphere and in laboratory studies. Since the dynamics of transfer of gases to particles has been presented in great detail by Hidy and Brock (1970), only general features will be reviewed here. The controlling mass transfer processes can be identified through their relaxation times (see glossary), which are:

a. the interparticle diffusion relaxation time, τ_{pp}

$$\tau_{pp} = N^{-2/3} D_{i,air}^{-1} \qquad (2\text{-}52)$$

which is a measure of the time required for a cloud of particles to attain a uniform vapor concentration of species i, where only molecular diffusion is important.

b. the diffusion to a single particle, τ_{sp}

$$\tau_{sp} = R^2 D_{i,air}^{-1}, \ Kn << 1 \qquad (2\text{-}53)$$

or

$$\tau_{sp} = R\bar{v}_i^{-1}, \ Kn << 1 \qquad (2\text{-}54)$$

which is a measure of the time required for transport of species i to a single particle in a stagnant gas, where only molecular diffusion is important.

c. the momentum to a single particle, τ_m

$$\tau_m = R\,u_o^{-1} \qquad (2\text{-}55)$$

which is the characteristic time for transport on momentum to a particle by fluid motion.

$$\tau_{sp} \cdot \tau_m^{-1} = Pe \qquad (2\text{-}56)$$

where Pe is the Péclét number and is given by

$$Pe = \text{fluid velocity} \times R \times D_{i,air}^{-1}. \qquad (2\text{-}57)$$

The Péclét number represents the ratio of convective and diffusion transport of gases to a particle. When this value is << 1, the mass transport relaxation times are governed by molecular diffusion; however, for larger values, fluid convection is significant and τ_{pp} and τ_{sp} will be reduced,

where

N = particle number concentration, cm^{-3}
$D_{i,air}$ = gaseous diffusion coefficient of species i in air, cm^2/sec
R = radius of particle, cm
$\bar{v}_i$ = the molecular mean speed of species i in air, cm/sec
u_o = the relative speed between the particle and air, cm/sec
Kn = Knudsen number = mean free path of air/R.

For particles with radius $R < 10\mu m$ and a maximum number concentration $N \lesssim 10^6 cm^{-3}$, the relaxation times are

$$\tau_{sp} \lesssim \tau_m \lesssim \tau_{pp} \lesssim 10^{-3} sec,$$

which has this meaning: The magnitude of a perturbation in the concentration of gaseous species i will be reduced by 1/e at time = τ. Thus, in the case stated above, which is reasonable for lower tropospheric aerosols, stationary conditions in the gas phase will be achieved in less than 10^{-3} sec.

The relaxation time τ_a for adsorption and solution at clean surfaces may be on the order of that for relaxation of internal molecular energy, which is very small compared to τ_{sp}. However, as mentioned in 2.4.2.2.3, surface films may significantly retard mass transfer between the air and aqueous phase. The mechanism and the magnitude of the effect is not established; probably, the phenomenon is due to the organic molecules in the film aligning to present their hydrophobic (paraffinic) parts to the air interface. Thus, the droplet takes on a "paraffinic" type surface, which will exhibit a much lower condensation coefficient than clean water surfaces to polar molecules such as H_2O, NH_3, and SO_2. The only relevant studies of the influence of organic surface films on τ_a have been conducted for the mass transfer of H_2O molecules from the aqueous solution droplets to air (see Section 2.4.2.2.3). The significance of such films in reducing τ_a for SO_2 and NH_3 have not been studied. However, the effect has been proposed by Junge and Scheich (1971) to explain their observations of the simultaneous presence of H_2SO_4 droplets and NH_3 in London. If organic surface films are able to reduce τ_a to $\gtrsim 5$ sec for absorption and subsequent reaction of NH_3 in the breath by H_2SO_4 droplets, then their inhalation and deposition in the lungs may pose serious health threats to humans.

For chemical reactions occurring in aqueous droplets, the diffusional transfer of the reactants must be considered. The diffusion relaxation time for reacting species i in the absence of internal circulation is (Lamb, 1945):

$$\tau_{\ell D} = \ell^2/D_{i,\,aq} \text{ (with no internal circulation)} \qquad (2\text{-}58)$$

where

ℓ = the thickness of the aqueous film on the particle, or the diameter of the aqueous droplet

$D_{i,aq}$ = diffusion coefficient of species i in the aqueous solution.

Since atmospheric particles are normally not subjected to forces that would maintain oscillation or deformation of small droplets, internal circulation needs to be considered only for droplets with diameter $\gtrsim$ 10 μm. For droplets with internal circulation:

$$\tau_{\ell D} = 10^{-4}\text{cm sec } R^{-1} \quad \text{(with internal circulation).} \qquad (2\text{-}59)$$

Thus, the diffusional relaxation time of reactants for likely tropospheric droplets is expected to be $\tau_{\ell D} < 0.1$ sec.

For aqueous particles with diameters less than 1 μm, the mass transport processes of reacting gases have relaxation times $\tau \lesssim 10^{-3}$ sec, except possibly for τ_a for transfer through an organic film-air interface. If the reactant half-lives are much less than the diffusional relaxation time, then the droplets may be viewed as homogeneous reactors whose feedstock rate is controlled by the mass transfer through the interface. Otherwise, the effects of chemical gradients in the droplet and in the surrounding air must be included (Satterfield, 1970).

2.4.4.2 Sulfuric Acid-Water Growth Dynamics--The growth rate of 100 percent H_2SO_4 submicrometer droplets suddenly exposed to humidified gas streams has been measured (Carabine and Maddock, 1976); it was found that the growth ended when the water vapor equilibrium was reached in <6 sec. Calculations that ignore the dissipation of the heat of dilution of the droplet predict growth times of 10^{-5} to 10^{-2} sec. Gentry and Brock (1968) have performed mass/heat transfer calculations for 0.1 μm diameter, 1.0M H_2SO_4 droplets and found that the heat transfer dominated the growth rate, causing it to be much less than expected from assuming isothermal conditions. Azarniouch et al. (1973) have performed similar calculations for supermicrometer H_2SO_4 droplets and have also deduced that heat transfer significantly reduces the growth rate. Thus, it is reasonable to expect that inhaled concentrated H_2SO_4 droplets may require a period of $\lesssim$6 sec. to attain their terminal size (governed by the relative humidity in the lungs) and final dilution.

2.4.4.3 Dynamics of Growth by Chemical Reaction--Few studies have been reported on the chemical reaction rate for gases and particles that are of interest in the lower troposphere. Attempts to measure the SO_2 oxidation rate in free and supported droplets were discussed in Section 2.3.4. Because of the attendant problems of the inability to separate collected droplets from the outflow stream of the reactor for free-droplet studies and possible radical termination at solid surfaces for supported droplets, those studies cannot be accepted as reliable for estimating mass transfer rates. At this time, the only reaction kinetics studies for gases and suspended droplets that are applicable to the lower troposphere are those for the $NH_{3(g)}$ - H_2SO_4 droplet system (Robbins and Cadle, 1957; Cadle and Robbins, 1960; Huntzicker et al., 1980). Using 98 percent and 12 percent H_2SO_4 droplets with diameters 0.2 to 0.9 μm, Robbins and Cadle (1957) observed that the reaction of NH_3 with the 98 percent H_2SO_4 droplets was not diffusion controlled, whereas the reaction with 12 percent H_2SO_4 was. They interpreted the slower reaction rate for the 98 percent H_2SO_4 droplets (10 percent of the collisions of NH_3 were effective) in terms of surface adsorption followed by the formation of an activated complex that transmitted the NH_3 through the interface. For the 12 percent H_2SO_4, 100 percent of the NH_3 collisions were effective. They did not consider the influence on growth time of heat transfer and formation of solid $(NH_4)_2SO_4$ as a surface crust; both of these should be expected to be important in reducing the growth time of concentrated H_2SO_4 droplets. Huntzicker et al. (1980) investigated the reaction for 0.3 to 1.4 μm H_2SO_4 droplets at 8 to 80 percent relative humidity; they found that the rates were between 21 to 70 percent of the diffusion-limited theoretical rate. They interpreted this range of rates, in addition to the observed decrease in rate as a function of time for low relative humidity, to indicate the accumulation reaction product on the surface. Possible heat transfer efforts were not considered. Cadle and Robbins (1960) also observed a reaction between NO_2 and NaCl solution droplets that was too fast to measure; the products were $NaNO_3$ droplets and $HCl_{(g)}$.

No kinetic studies relevant to tropospheric conditions have been reported for gases reacting with solid particles. In Section 2.3.4, the works of Smith et al. (1969), Chun and Quon (1973), Siegel, et al. (1974), and Judeikis et al. (1978) were mentioned. The work of Judeikis and coworkers is of most interest because their reactor design permitted them to estimate the effectiveness of gas collisions for reacting. They investigated the collision effectiveness ϕ of SO_2, NO_2, O_3, and CO on a variety of materials, including metal oxides, salts, charcoal, cement, fly ash, and sand. SO_2 and NO_2 exhibited high reaction rates with most materials. Unfortunately, the highest collision efficiency leading to reaction that they could measure was $\phi \lesssim 10^{-4}$. (The value for a water molecule condensing on a water droplet is $\phi < 10^{-3}$; for such values of $\phi \gtrsim 10^{-4}$, there is little difference for gas-particle reaction rates in the lower troposphere if $\sim 10^{-3} < \phi < 1$.)

2.4.4.4 Dynamics of Desorption--No kinetics for desorption of NH_3 or SO_2 have been reported for aqueous droplets under conditions that are relevant to the lower troposphere. The results of Smith et al. (1969) are of interest in that they demonstrated that SO_2 is transported by particles and undergoes desorption in a tube designed to remove SO_2 at a reactive wall. Unfortunately, the surfaces of the particles were incompletely characterized; it is not known if the SO_2 was physisorbed or dissolved in thin surface films.

It is reasonable that the affinity of dissolved SO_2 and its hydrated products (HSO_3^- and SO_3^{2-}) in droplets that are inhaled may be increased by basification by NH_3 in the lungs; in such cases, the dissolved SO_2 would be transported by fine droplets much deeper into the lungs than gaseous SO_2 can penetrate. Presently, there are insufficient studies of the mass transport of dissolved SO_2 in the presence of NH_3 and reactive walls to verify this picture.

In summary:

1. The transfer of reactive gases to lower tropospheric and urban particles is known, with the exception of the possible role of organic films.
2. The growth rate of H_2SO_4 droplets suddenly exposed to high humidity has been demonstrated by experiments and theory to be dependent on the heat transfer rate. The nonisothermal growth rates are several orders of magnitude greater than those predicted assuming heat transfer to be unimportant.
3. Few gas-particle chemical reactions relevant to the lower troposphere have been reported, which is hindering the testing of theory.
4. No quantitative investigations of SO_2 or NH_3 desorption from particles under conditions relevant to the lower troposphere have been reported. One study indicates that SO_2 may be carried (as sorbed species) on particles through tubes with reactive walls in mcuh greater quantities than gaseous SO_2 can penetrate.

2.4.5 Characterization of Atmospheric Aerosol

Significant advances have been made in the past decade in regard to elucidating the nature of the tropospheric particle size, area, volume, and mass distribution functions and the chemical composition. This section will discuss general aspects of distribution functions, the observed behavior of urban particle distributions, and chemical composition. Evidence will be presented for the existence of multimodal mass distributions and the difference in composition of urban coarse and fine particles separated at about 2 µm, but it is not a sharp division of the chemical composition. One of the major reasons for selecting 2.5 µm as the separation point is that it occurs in the region of the minimum between the accumulation (fine) mode and the coarse particle mode in volume (or mass) distributions of urban particles. However, nonurban particles may not have volume (or mass) distributions that resemble those of urban environments; in such cases, a separation at 2.5 µm may not yield differences in composition (see Figure 1-1).

2.4.5.1 Distribution--The multimodal nature (to be discussed below) of tropospheric particle surface and mass distribution functions remained unrecognized until the early 1970's largely because of the methods used to present number, size and mass distribution data.

Tropospheric particles are polydisperse. For reason of convenience, particle number (N), area (A), volume (V), and mass (M) concentration data are usually expressed in terms of a mathematical distribution function of diameter (D). Such functions are ordinarily characterized by two parameters. The fraction of the total number of particles having diameters which lie between D and dD is:

$$dN = f(D)dD \qquad (2\text{-}60)$$

with the normalization condition:

$$\int_0^\infty f(D)dD = 1. \qquad (2\text{-}61)$$

The curve representing the function f(D) is called the "number frequency distribution" or the "number differential" curve. Similarly, the area and volume frequency distributions are:

$$dA = f(D^2)dD \qquad (2\text{-}62)$$

and

$$dV = f(D^3)dD \qquad (2\text{-}63)$$

where the proper normalization is taken into account.

Prior to the 1970's, atmospheric scientists employed two predominant types of frequency distributions [i.e., functional forms of f(D), $f(D^2)$, and $f(D^3)$]. They were (a) Junge's (1955) power law distribution for particle size and (b) the log-normal distribution for mass.

Investigators who used instrumentation to measure particle size spectra usually reported their data in terms of Junge's (1955) power law, which is:

$$\frac{dN}{dD} = AD^{-k} \qquad (2\text{-}64)$$

where A and k are constants. Clark and Whitby (1967) found that this power law was a reasonable fit to the number distribution, but it was an inadequate model of the surface and volume distribution.

Also, investigators who used cascade impactors to determine the mass distribution spectra usually reported their data in terms of the log-normal distribution (see Fuchs, 1964; Cadle, 1975). While multimodal log-normal distributions can be recognized from standard plots of data on log-normal graph paper, three effects combined to mask the multimodal character of urban particle mass distribution: (1) the cascade impactors had serious (and unknown) inlet biases against particles larger than about 5 µm, (2) the cascade impactors did not have operational characteristics that permitted mass fractionation below about 0.2 µm, and (3) particle bounce distorts the mass distribution in cascade impactors. A warning by Fuchs (1964) that the log-normal distribution is an adequate model only if the particles are sampled perfectly and the sampler provides adequate fractionation points went unnoticed.

Whitby et al. (1972) were responsible for a major advance in recognizing that Junge's (1955) power law and the log-normal distribution function were inadequate models of experimental data for urban aerosols. Instead of seeking other functional forms to express the number, area, and volume distribution, they plotted dN/d log D, dA/d log D, and dV/d log D versus log D. The result is seen in Figure 2-12. This type of plot has a convenient feature: The area under the curve is proportional to the quantity (N, A, or V) between two diameters. The particle volume between the diameters D_1 and D_2 is:

$$V(D_1, D_2) = \int_{\log D_1}^{\log D_2} (dV/d \log D)\, d \log D \qquad (2\text{-}65)$$

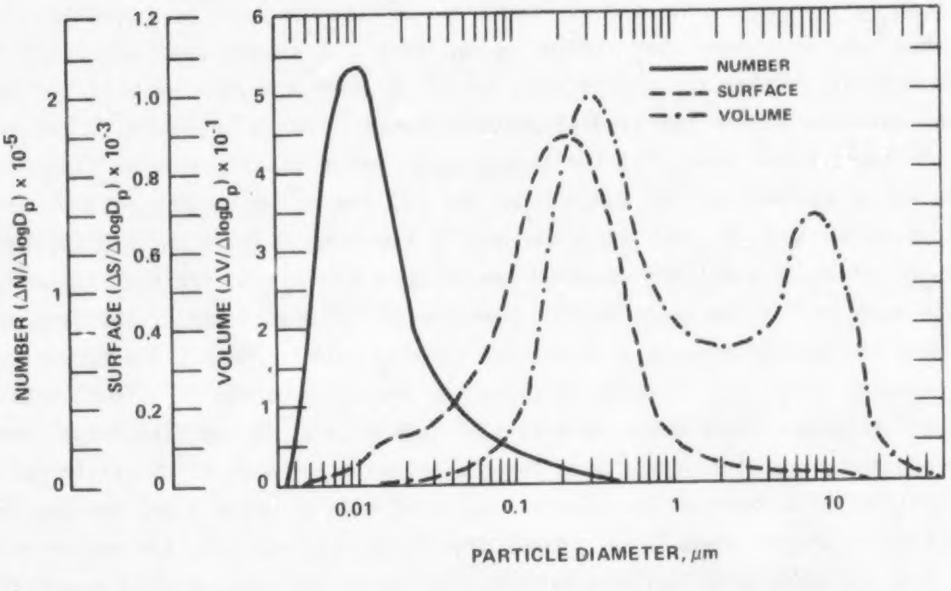

Figure 2-12. Frequency plots of number, surface, and volume distributions for 1969 Pasadena smog aerosol.

Source: Whitby, in National Academy of Sciences (NAS), Airborne Particles, (1977).

For small values of Δ log D, Equation 2-47 becomes

$$V(D_1, D_2) = \overline{(\Delta V/\Delta \log D)} \times \Delta \log D \qquad (2\text{-}66)$$

where $\overline{(\Delta V/\Delta \log D)}$ is the average value in the interval between log D_1 and log D_2.

The peaks in the three types of distribution plots are called modes. As is evident in Figure 2-12, there is usually one number mode, one or two surface modes, and two volume modes for urban aerosols; sometimes an additional volume mode is observed in the range from 0.005 to 0.05 µm when a strong source of fresh nuclei is close to the sampling site. In strict usage, a mode is a single point which is a maximum in a frequency distribution; however, aerosol investigators have often used it to represent the integral of the distribution between the minima on each side of the maximum. For example, the particle volume distribution in Figure 2-12 has maxima (modes) at 0.3 and 8 µm. However, the integral of the particle volume frequency distribution with a maximum at 0.3 µm and minima at ~0.02 µm and ~2 µm is commonly called the accumulation mode. The use of "mode" to denote integrals over specific limits is unfortunate, but now so common that change is unlikely. A reader must determine from the context of an article whether the author uses "mode" to mean a single point or an integral.

The urban particle volume (mass) distribution generally has 2 or 3 modes. The integrals associated with these modes are: (1) the coarse mode, which usually extends from ~2-3 µm to ~100 µm, and has a maximum in the range 5-50 µm; (2) the accumulation mode, which usually extends from ~0.02 to ~1-5 µm, and has a maximum in the range 0.1-1.0 µm; and (3) the Aitken (or nuclei) mode, which is sometimes observed near a strong source of fresh nuclei and extends from ~0.005 to 0.05 µm. These modes result from the differences in major source types. The coarse mode consists mainly of primary particles such as mineral dust. The accumulation and Aitken modes consist of primary combustion smoke and secondary particles. The limitations of particle growth processes cause these particles to "accumulate" in the size range from 0.2 to 2 µm. The minimum between the coarse mode and the accumulation mode is generally not at zero on the distribution curve because the mineral dust size extends below 1 µm, and the growth of secondary particles extends above 3 µm. Also, the minima may shift in the region of 1-5 µm. In spite of this behavior, the minimum between the coarse and accumulation modes offers an attractive position to fractionate particle samples for health and welfare considerations. However, it must be recognized that this mode of the urban particle volume (or mass) distribution is an idealization. The chemical separation between the accumulation mode (integral) and the coarse mode (integral) is not sharp. Figure 2-13 shows the more general picture of the volume (or mass) distributions for a variety of types of locations and conditions that range from urban to mountain background. It is important to note the influence of combustion sources, secondary sources, natural sources, windspeed, and turbulence on the volume distribution. It is obvious that the distributions observed at a site will be a composite of these, and it may exhibit a large degree of fluctuation among the components. Thus, the relative

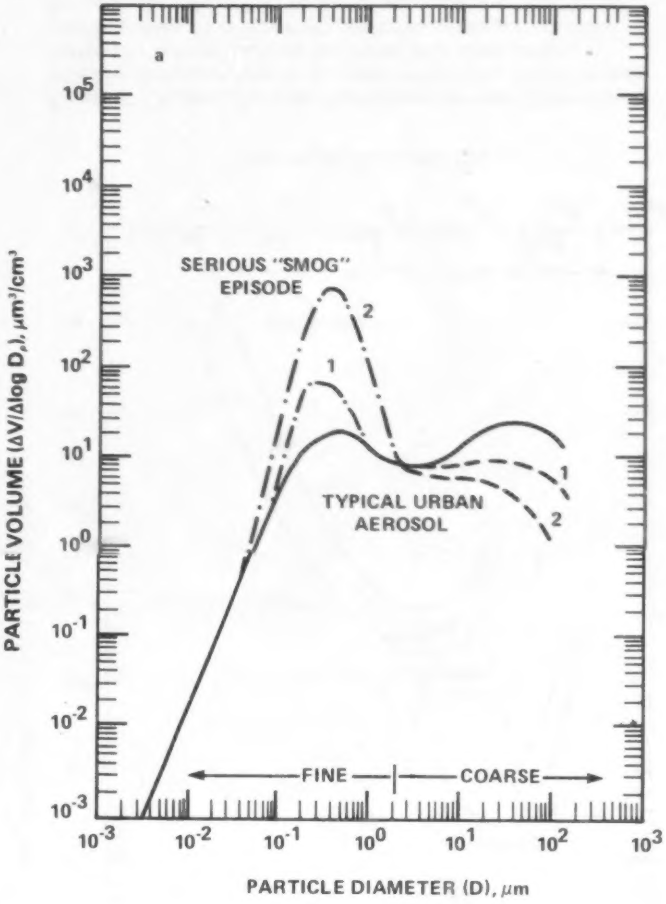

Figure 2-13a. Idealized size distribution for particles found in typical urban aerosols (mainly from anthropogenic sources) under varying weather conditions. Note bimodal distribution under usual conditions and shift in distribution (increasing fine-mode particles, decreasing coarse-mode particles) under stagnation (1) and serious "smog" conditions, (2), respectively.

Source: Adapted from Slinn (1976).

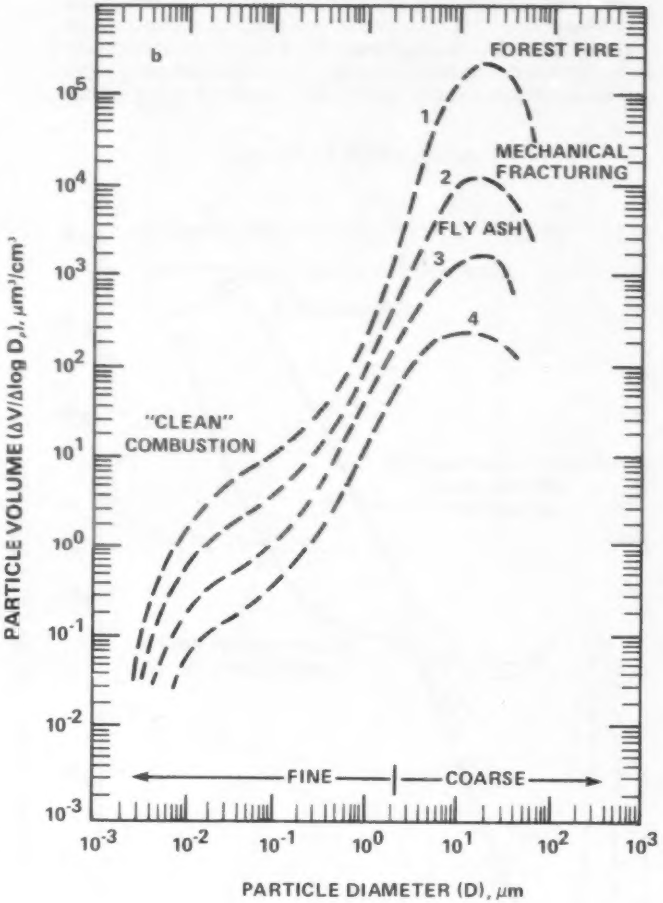

Figure 2-13b. Idealized size distribution for atmospheric particles from anthropogenic sources, showing fine particle contributions from "clean" high-temperature combustion, and coarse particle contributions from "dirty" fly ash sources, forest fires, and crushing and grinding operations. Note change in distribution near sources (1) and at increasing distances (2,3,4) from sources.

Source: Adapted from Slinn (1976).

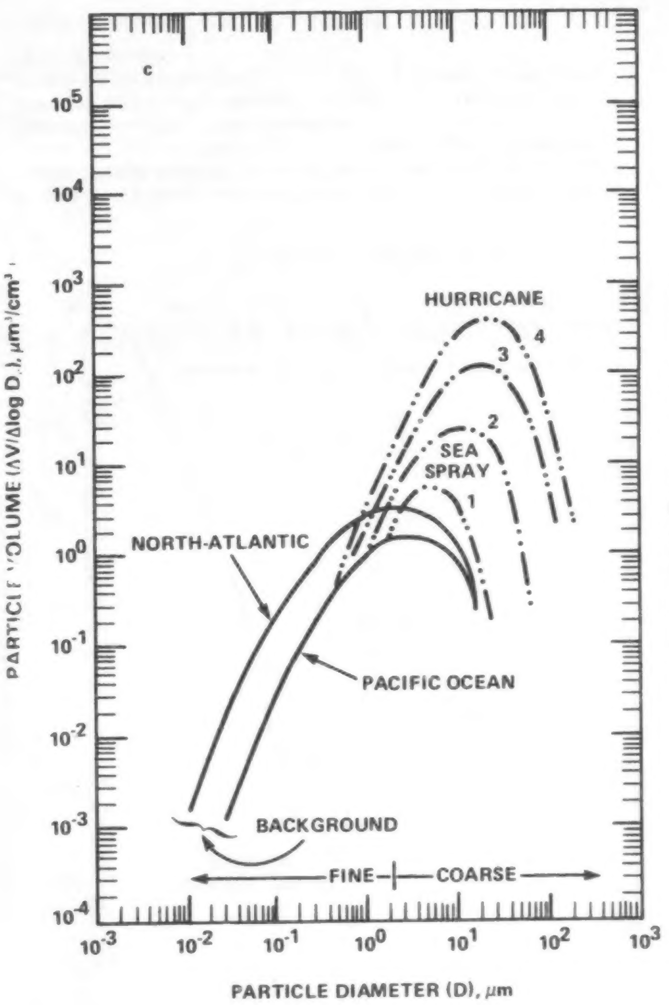

Figure 2-13c. Idealized size distribution for atmospheric particles from natural sources in a marine setting. Note, in comparison to typical background levels over open ocean, increasing levels of coarse-mode particles ranging from those found in sea spray (1,2) to the extreme cases of storms (3) and hurricanes (4).

Source: Adapted from Slinn (1976).

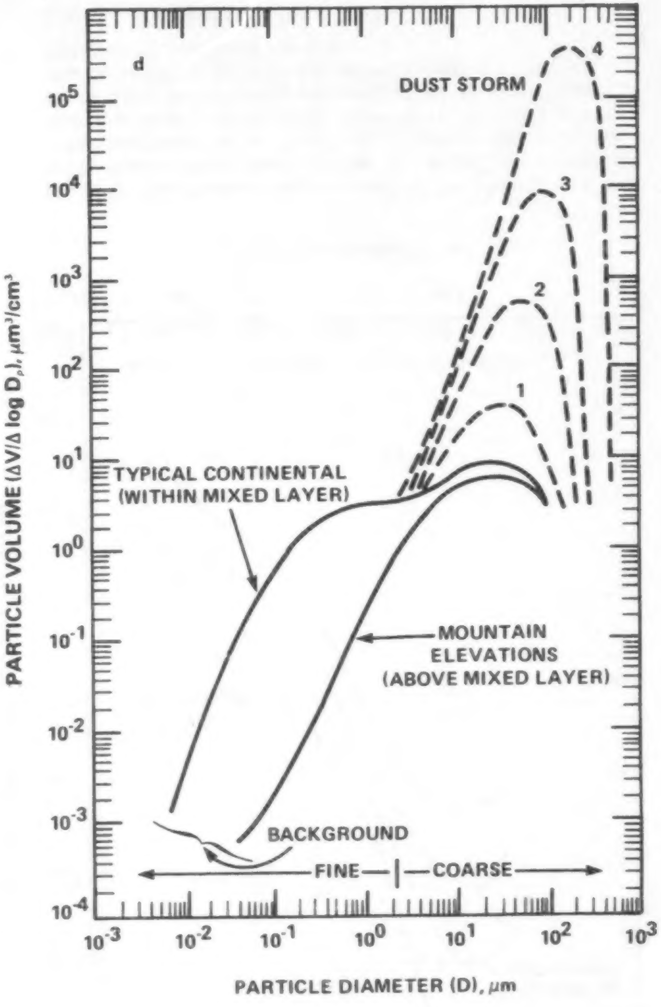

Figure 2-13d. Idealized size distribution for atmospheric particles from natural sources in a continental setting. Note, in comparison to usual background profiles over typical continental and high-elevation mountain areas, increasing contributions of coarse-mode particles from wind-blown dusts (1,2,3), ranging to the extreme case of a dust storm (4).

Source: Adapted from Slinn (1976).

magnitudes of the Aitken, acculation, and coarse mode integrals will vary in an uncorrelated manner, as will the degree of goodness of the chemical separation of these mode integrals.

Samplers have been devised to collect the particles into two size fractions (coarse and fine) with a separation diameter in the range of 1-5 μm. The coarse fraction is the mass with aerodynamic diameter between the separation and the inlet cutoff diameters. Therefore, the coarse fraction is the portion of the coarse mode that lies between these aerodynamic diameters. The fine fraction is the mass with aerodynamic diameter less than the separation point; it usually corresponds approximately to the sum of the accumulation and Aitken modes. A variety of separation diameters in the range of 1-5 μm and inlet cutoff diameters greater than 10 μm have been used.

Multimodal distributions generally are observed for urban aerosols but may not be detected in other cases, e.g., marine environments or areas dominated by a strong source.

In summary:

1. The particle volume (or mass) frequency function ($\Delta V/\Delta \log D$ versus $\log D$) is often multimodal. The fine-volume fraction may have two or more modes at ~0.02 and ~0.2 μm. The coarse fraction generally has one mode within the range ~5 - 50 μm.
2. The types of sources that contribute particles to the fine and to the coarse fractions are relatively well known.
3. The particle volume frequency functions for the fine and for the coarse fractions often behave independently.

2.4.5.2 Composition of Particles--Upon elucidating the multimodal behavior of particle distributions through the use of the forms $\Delta N/\Delta \log D$, $\Delta S/\Delta \log D$, and $\Delta V/\Delta \log D$, it was recognized that the chemical composition of urban particles in the coarse fraction is different from that in the fine fraction (with a separation diameter of 1-3 μm). Evidence is cited in Table 2-22, which shows that tropospheric secondary particles containing SO_4^{2-}, NH_4^+, H^+, and organics are in the fine fraction, while primary particles consisting principally of basic minerals are in the coarse fraction. The composition of the fine and coarse fractions are shown in Figure 2-14, which is an idealization of the bimodal mass distribution. As pointed out in Section 2.4.5.1, the accumulation and coarse mode integrals are not sharply divided. Thus, the separation point for the fine and coarse modes does not neatly divide the particles by chemical composition.

Investigations of the chemical composition of the fine and coarse particles for urban aerosols indicate that chemical species may be distributed mainly in the fine or coarse fraction, or both, as is shown in Table 2-22. The major components of the fine fraction of urban particles are SO_4^{2-}, NH_4^+, NO_3^-, Pb compounds, elemental C (soot), and condensed organic matter. In Sections 5.5 and 5.6, the composition of the fine and coarse fractions and their acidity characteristics are discussed in more detail.

2.4.5.2.1 Elemental carbon (soot) and organics. The carbon in fine particles consists of an elemental component (such as graphite or soot) and an organic component of low volatility.

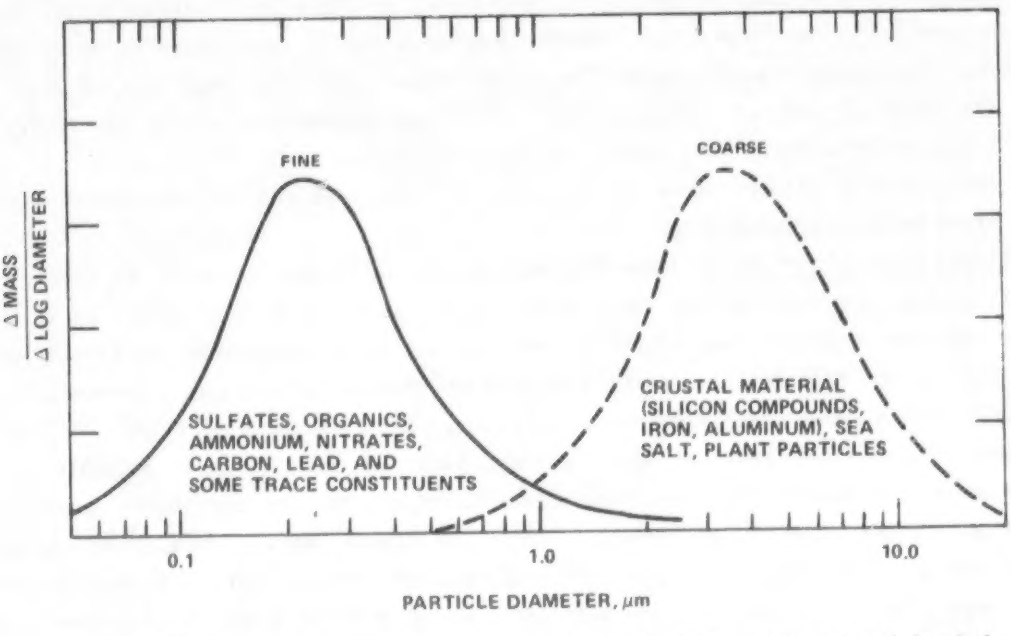

Figure 2-14. Idealized representation of typical fine- and coarse-particle mass and chemical composition distribution in an urban aerosol. Although some overlap exists, note substantial differences in chemical composition of fine versus coarse modes. Chemical species of each mode are listed in approximate order of relative mass contribution. Note that the ordinate is linear and not logarithmic.

TABLE 2-22. CLASSIFICATION OF MAJOR CHEMICAL SPECIES ASSOCIATED WITH ATMOSPHERIC PARTICLES

Fine Fraction	Coarse Fraction	Both Fine and Coarse Fractions	Variable
SO_4^{2-}, C (soot), organic (condensed vapors), Pb, NH_4^+, As, Se, H^+, acids	Fe, Ca, Ti, Mg, K, PO_4^{3-}, Si, Al, organic (pollen, spores, plant parts), bases	NO_3^-, Cl^-	Zn, Cu, Ni, Mn Sn, Cd, V, Sb

Sources: Lee and Goranson (1976); Patterson and Wagman (1977); Durham et al. (1975); Rahn et al. (1971); Akselsson et al. (1975); Hardy et al. (1976); Gladney et al. (1974); Lundgren and Paulus (1975); Lee et al. (1968); Lee et al. (1972).

There are significant differences in the optical properties of elemental and organic carbon components. Elemental carbon is formed during the combustion of fossil fuels and is emitted as primary particles (~0.1 μm), which strongly absorb light. The organic component consists of primary hydrocarbons emitted in combustion exhaust and of secondary organics formed by photochemical reactions. These primary hydrocarbons and secondary organic vapors either nucleate or condense on existing aerosols. They do not strongly absorb light, but do contribute to light scattering in urban hazes.

There are only limited data on the mass ratio of elemental/(primary + secondary organics) for a few cities. Appel et al. (1978, 1979) found that for a 4-day period in July 1975 elemental carbon was the most abundant carbon species in Pasadena, Pomona, and Riverside. Also, the concentration of secondary organic carbon was usually twice that of primary hydrocarbons. Of the secondary organics, hexanedioic and pentanedioic acids were among the most abundant products; most likely they were oxidation products of cyclohexene and cyclopentene emitted by motor vehicles. The composition of the organic component retained on filters varied with the length of the sampling period. The retention of less polar organics (e.g., hydrocarbons) was favored by longer sampling time, apparently because of adsorption of such organics on previously collected material. From total carbon, benzene soluble organics, and hydrogen analyses of fine particles collected in Denver in November 1971, it was estimated that the elemental carbon was 2.3-3.6 $\mu g/m^3$ for the episode days observed; using Pb concentration as a tracer, it was suggested that in November 1973 in Denver the elemental carbon in fine particles was 1.7 - 4.4 $\mu g/m^3$ (Durham et al., 1979). Also, for Denver in November 1973, Pierson and Russell (1979) estimated from high-volume samples the total elemental carbon to be 2.9 - 27.6 $\mu g/m^3$.

Although atmospheric measurements of carbon-containing particles are less complete than those of sulfates, available results suggest that carbon-containing particles in many locations, both urban and nonurban, are the second most abundant fine-particle species after sulfates. At some western urban locations where SO_x emissions have been small, carbon-containing aerosols have made the largest contribution to fine-particle mass. The concentration of primary carbonaceous particles is likely to have been even higher in the past in the Eastern United States when coal was more widely used as a fuel. With the growing use of industrial coal and wood combustors for home heating, carbonaceous particle concentrations are likely to increase.

Grosjean (1977) has extensively reviewed the methods of primary and secondary organic particle identification, and the physical and chemical aspects of their formation. Primary organics emitted into the atmosphere by industrial sources, motor vehicles, agricultural activities, and natural sources include: linear and branched alkanes and alkenes, substituted benzenes and styrenes, quinones, acridines, quinolines, phenols, cresols, phthalates, fatty acids, carbonyl compounds, polyaromatic hydrocarbons, terpenes, and pesticides. Secondary organic particles are formed by the oxidation reactions of the primary organics, ozone, and nitrogen oxides. Typical products that have been identified are: aliphatic organic nitrates, dicarboxylic acids, benzoic and phenylacetic acids, and terpene products such as pinonic acid (Grosjean and Friedlander, 1975; Miller et al., 1972; Schuetzle et al., 1975). By using computer-controlled high-resolution mass spectrometry and thermal analysis Schuetzle et al. (1975) and Cronn et al. (1977) obtained diurnal variations of primary and secondary organics from 2-hour size-resolved samples.

In an attempt to understand the atmospheric oxidation pathways that yield secondary organic particles, simple mixtures have been investigated in laboratory chamber studies. As discussed in more detail by Grosjean (1977), the following trends have been observed by chamber researchers: (a) most paraffins do not generate aerosols during irradiation, (b) acetylenes do not form aerosols, (c) all other unsaturated compounds with six or more carbon atoms can form organic aerosols, (d) cyclic olefins and diolefins form more aerosol than their 1-alkene analogs, (e) conflicting results have been reported on the aerosol-forming ability of aromatics, (f) carbonyl compounds do not generate aerosol, and (g) mechanical stirring inhibits particle formation. Cyclic olefins are the most efficient class of organic particle precursors, due mainly to their high gas-phase reactivity and their ability to form nonvolatile dicarboxylic acids.

The chemical composition of organic particles generated in smog chambers is not well established for suspected important aerosol precursors. Functional group analyses for the products of olefins, benzene and benzene-substituted compounds, and terpenes that have reacted with ozone and nitrogen oxides show that the bulk consists of highly oxygenated compounds, which include carbonyls, carboxylic acids, and nitrate esters. Only a few studies of species identification have been reported. Detailed aerosol product identification has been reported for the ozone-1-butene reaction (Lipeles et al., 1973); the NO_x-toluene, NO_x-cyclohexene, and NO_x-α-pinene photoreactions (Schwartz, 1974), and the NO_x-cyclopentene, NO_x-cyclohexene, and 1-7-octadiene photoreactions (Grosjean, 1977). Good agreement was indicated by Grosjean (1977) with Schwartz (1974) for the NO_x-cyclohexene photoreaction, except that Grosjean observed hexanedioic acid to be the major product (not reported by Schwartz). It is significant that most of the polyfunctional compounds identified (see the cited papers and the NAS report for details) have also been identified as important constituents in ambient aerosols.

The secondary particles formed form alkenes having seven or more carbons (cyclic olefins, diolefins, and terpenes) grow into the light-scattering range and produce appreciable visibility reduction. For example, particles formed from cyclic olefins and diolefins have particle sizes between 0.1 and 0.3 µm. For such systems, the gas-to-particle conversion process consists of the formation of the supersaturation of the gas phase and subsequent condensation on preexisting particles.

The rates of conversion of precursor organic vapors to organic particles in Los Angeles have been estimated to average 1 to 2 percent per hour. This moderate rate of conversion is consistent with the observation (see Grosjean, 1977) that organics account for an important fraction of the fine particles under conditions of intense photochemical activity, while only a small part of the precursor organic vapors are converted to particulate matter.

2.4.5.2.2 Nitrates. Nitrogen oxide gases are oxidized in the atmosphere to yield HNO_3, which accumulates as nitrate in both fine and coarse particles. Because the topics related to the transport of nitrogen oxides and their transformation to gaseous and particulate nitrates are discussed in the document Air Quality Criteria for Oxides of Nitrogen (U.S. EPA, 1982), they will not be repeated here. (These topics include visibility, environmental transport and transformation, and acidic precipitation.) Atmospheric nitrates most likely result from photochemical reactions involving the oxidation of NO and NO_2 to yield HNO_3 and organic nitrates (Demerjian et al., 1974). The measurement of ambient nitrate particles has been recognized to be subject to significant sampling errors, which are discussed in Chapter 3.

In summary:

1. The composition of the coarse fraction of continental tropospheric particles is dominated by primary minerals.
2. The composition of the fine fraction of continental tropospheric particles is dominated by secondary particles that consist mainly of SO_4^{2-}, NO_3^-, NH_4^+, H^+, and organics, plus primary elemental soot.
3. The fine fraction is often acidic, and the coarse fraction is often basic.
4. The chemical pathways for forming organics and NO_3^- particles are not fully understood.

2.4.6 Particle-Size Spectrum Evolution

The evolution of the atmospheric particle-size distribution spectra can be related in principle to pollution sources through the "general dynamic equation" (GDE). The form of the GDE is complex, requiring the application of sophisticated numerical techniques to obtain solutions through the use of large computers. Since the application of the GDE requires the detailed knowledge of all processes significantly influencing particle formation, growth, and removal, its main application to date has been to simulate simple model systems. In a few cases, simulation results have been compared to smog chamber and atmospheric observations. While this type of research is active, progress has been slowed due to the lack of knowledge of the important pathways and chemical rates for forming sulfate, nitrate, and organic particles in the atmosphere. Another limitation is imposed by the incomplete knowledge of the relation between atmospheric turbulence and particle dynamics. In this section, the GDE will be presented and recent studies identified in which it has been applied.

2.4.6.1 General Dynamic Equation (GDE)--The evolution of the particle size/composition distribution spectra is given by the nonlinear, partial integro-differential equation (Brock, 1976; Friedlander, 1977; Gelbard and Seinfeld, 1978):

$$\begin{aligned} \partial n_k/\partial t + \nabla\cdot n_k\underline{v} &= \nabla\cdot\bar{\bar{K}}\nabla n_k + [\partial n_k/\partial t]_{growth} \\ &+ [\partial n_k/\partial t]_{coag} + \sum_{P} \varepsilon_P(k) \\ &+ \sum_{i} \varepsilon_{N_i} - \nabla\cdot\underline{c}n_k \end{aligned} \qquad (2\text{-}67)$$

where

n_k = the number concentration of particles of type "k" at a specific point $\underline{r}$ in space at time t, $(\underline{r},t)$

$\underline{v}$ = the fluid velocity

$\bar{\bar{K}}$ = eddy diffusivity tensor

$\varepsilon_P(k)$ = rate of input at $(\underline{r},t)$ of k-type particles from primary source P

εN_i = rate of production of particles at $(\underline{r},t)$ by homogeneous nucleation of the i-th chemical species

$\underline{c}$ = particle velocity resulting from external force field (such as gravity).

In words, the equation has the following meaning:

rate of change in composition or in size distribution + particle transport with velocity $\underline{v}$ (advection)

= particle transport due to dispersion (convection) + rate of change (growth) due to condensation and chemical reactions in particles

+ rate of change due to coagulation + rate of change due to input from primary sources

+ rate of change due to homogeneous nucleation + rate of change from external force field (sedimentation).

2.4.6.2 Application of the GDE--Through the use of the GDE, it is possible to describe simultaneously and quantitatively particle interactions, gas-to-particle conversions, nucleation, and sedimentation. The GDE can be used as a module in atmospheric K-theory transport/transformation models that may include: (a) primary point, line, and area sources, and (b) gas-phase photochemistry, producing low-vapor pressure products that condense on existing particles or nucleate new ones. Because of computer limitations and lack of knowledge of all the pathways, the GDE has usually been applied by making many simplifications. Many of the studies and the features of the GDE that they retained are shown in Table 2-23. These studies have been classified as (a) Growth Laws, (b) Complex Simulations, (c) Comparisons with Chamber Observations, and (d) Comparisons with Atmospheric Observations.

The "Growth Laws" studies deal with the differences in evolution of the size distribution due to condensation, chemical reactions on the particle surface, and chemical reactions in the particle. While the results of these calculations are enlightening, caution must be exercised in using them to infer atmospheric gas-to-particle pathways. The remaining processes that are ignored may not be stationary (especially "sources") and may significantly influence the particle size evolution.

The "Theoretical Complex Simulations" studies are those in which the investigators realized that processes other than "growth" of particles are important to the size distribution evolution. These studies demonstrated through theoretical calculations the relative roles of the processes considered in influencing the evolution. Again, caution is suggested in using the results to infer atmospheric pathways from simulations that do not incorporate processes known to be important in the atmosphere.

The "Comparisons with Chamber Observations" studies are useful for developing the growth, coagulation, and nucleation components of the investigators' GDE model. Table 2-23 references only those studies in which the investigators predicted the particle size evolution using the GDE. Takahashi (1970), using a non-chemically reactive system, obtained good agreement for

TABLE 2-23. APPLICATION OF GDE TO DESCRIBE PARTICLE SIZE EVOLUTION

Investigators	Condensation	Coagulation	Sources	Nucleation	External Forces	Advection	Convection
A. GROWTH LAWS							
Brock (1972)	√	√					
Seinfeld & Ramabhadran (1975)	√						
B. THEORETICAL COMPLEX SIMULATIONS							
Huang et al. (1970)		√			√		
Burgmeier et al. (1972)		√	√		√		
Wadden et al. (1974)	√	√			√		
Burgmeier & Blifford (1979)	√	√	√		√		
Chu & Seinfeld (1975)	√						
Ramabhadran et al. (1976)	√	√					
Middleton & Brock (1976)	√	√	√	√			
Kiang & Middleton (1977)	√	√		√			
Middleton & Brock (1977)	√	√	√		√	√	√
Sheih (1977)		√	√		√	√	√
Suck et al. (1977)	√	√	√		√		
Suck & Brock (1979)		√					
Crump & Seinfeld (1980)	√	√	√	√			
Tambour & Seinfeld (1980)		√					
Tsang & Brock (1982)		√	√			√	√

(continued)

TABLE 2-23 (continued)

Investigators	Condensation	Coagulation	Sources	Nucleation	External Forces	Advection	Convection
C. COMPARISONS WITH CHAMBER OBSERVATIONS							
Takahashi (1970)		✓	✓				
Heisler & Friedlander (1977)	✓						
Gelbard & Seinfeld (1979)	✓	✓	✓	✓			
McMurry (1980)	✓	✓	✓				
D. COMPARISONS WITH ATMOSPHERIC OBSERVATIONS							
Husar et al. (1972)	✓						
Heisler et al. (1973)	✓						
Husar & Whitby (1973)	✓						
Gartrell & Friedlander (1975)	✓						
Heisler & Friedlander (1977)	✓						
Suck et al. (1978)			✓		✓	✓	✓
Eltgroth & Hobbs (1979)	✓	✓	✓		✓	✓	✓
McMurry et al. (1981)	✓						
McMurry and Wilson (1982)	✓						

the evolution of the size distribution in a continuous-stirred tank reactor. Gelbard and Seinfeld (1979) were able to predict the condensation growth of pre-existing particles for McMurry's (1977) SO_2 photochemical oxidation/particle evolution measurements, but they were unable to predict new particle formation using the theory of binary nucleation. McMurry (1980) has reported good agreement between modeling results and the photochemical oxidation/particle evolution measurements of Clark (1972). He considered the condensation of monomers on small clusters of molecules and cluster coagulation. Heisler and Friedlander (1977) studied the gas-to-particle conversion of organics in photochemical smog. They concluded that their chamber results for particle evolution are explained by the gas-phase oxidation of organic gases to form low-vapor pressure molecules that condense on pre-existing particles. Their mechanism included the Kelvin effect, which restricted the growth to particles above a critical particle size. Heisler and Friedlander (1977) reported that this particle evolution mechanism yielded computed particle size distributions which agreed well with atmospheric measurements. Unfortunately, to date, GDE modeling comparisons with observations for more complex chemically reactive aerosol systems have not been reported.

The "Comparisons with Atmospheric Observations" studies referenced in Table 2-23 include only those for which the investigators predicted the particle size evolution using the GDE. Most of the studies included only particle evolution due to condensation growth and are not reviewed here. Suck et al. (1978) have used a 3-dimensional K-theory model with primary area sources to describe the transport and dry deposition of dust in Maricopa Co., AZ. They reported good agreement between predicted and observed suspended mass concentrations. McMurry et al. (1981) have used a 1-dimensional model to infer the evolution of the averaged crosswind particle size distribution. For the data they analyzed, they reported that about 80 percent of the particle volume formation could be accounted for by condensation growth. The most elaborate application of the GDE has been by Eltgroth and Hobbs (1979) for the evolution of particle size in coal-fired power plant plumes. They have combined a trace-gas chemistry scheme for SO_x, NO_x, hydrocarbons, and oxidants (35 reactions) with a particle scheme (GDE) including condensation, coagulation, gas-particle reactions, and sedimentation. These two schemes were used in a K-theory dispersion model to predict the 3-dimensional concentrations and size distributions. The model predicted the essential features of the plume reactions, including enhanced reactivity at the outer boundaries. They concluded that diffusion, coagulation, sedimentation, and condensation growth all are important to the particle size distribution evolution.

The GDE offers an attractive pathway to develop atmospheric aerosol models based on physico-chemical processes. An active area of research is to formulate such models on large computers and reduce their size through simplified representation of parameters to obtain versions that can be operated on smaller, more available computers. This derivative approach defines the useful range of parameters in relation to the phenomenologically correct parent model. The alternate pathway of directly formulating reduced parameter models to fit a limited number and type of field observations has been used, but those studies will not be reviewed here. It is difficult to define the useful range of the parameters of such models. In Summary:

1. The evolution of atmospheric particle-size distribution spectrum can be described by the GDE.
2. The application of the GDE requires detailed knowledge of all important processes. Often, such information is not known.
3. The GDE is suitable for use as a module in K-theory type dispersion models.
4. Most applications of the GDE have been made with extensive simplifications; however, comparisons with observations of several smog chamber and atmospheric studies have indicated good agreement.
5. The application of the GDE to relate sources and particle size distributions for the ultimate use in planning control strategies is an active area of research.

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3. TECHNIQUES FOR THE COLLECTION AND ANALYSIS OF SULFUR OXIDES, PARTICULATE MATTER, AND ACIDIC PRECIPITATION

3.1 INTRODUCTION

The 1969 and 1970 Air Quality Criteria documents for particulate matter (PM) and sulfur oxides (SO_x), respectively, (National Air Pollution Control Administration, 1969, 1970) provided a reasonably thorough review of measurement techniques available at that time. Subsequent advances in measurement technology for these pollutants have resulted in several new techniques and more information on the quality of data collected by older methods. This chapter provides a review and, where possible, a critical assessment of both the earlier techniques used in historical monitoring efforts and the newer techniques on which much of the information gathered in the next few years will be based.

Methods were selected for inclusion in this review based primarily on frequency of their use in past or current studies. These include routine monitoring applications used in demonstrating compliance with air quality standards; in support of effects studies, especially epidemiology; and in examining long-term trends for the evaluation of control strategy effectiveness. More widely used research measurement methods that have been used to collect important ancillary data, such as particle size distributions for aerosols, are also discussed but in less detail.

Measurement techniques for SO_x, PM, and acidic precipitation are governed by the chemical and physical properties of the substances to be measured. Since the chemistry and physics of SO_x and PM are discussed in detail in Chapter 2, and those of acidic precipitation in Chapters 6-8, only the measurement methods per se are discussed in this chapter. Chemical analysis methods for PM and acidic precipitation for constituents such as sulfates are described following the sections on methods of sample collection. The relationship of particles to visibility and their related measurements are discussed in Chapter 9.

Discussion of each sampling and analytical method covered in this chapter includes a general description, a discussion of the utility and applicability of the method, and, where information is available, a critical assessment of the method's capabilities. The capabilities described include accuracy, precision, measurement range, sensitivity to interferences, and reliability. The last parameter (reliability) is strongly influenced by competency of the operator and completeness of accepted procedure documents. Except in very specific cases, it is difficult to evaluate these factors and make conclusions about the general usefulness of the method. Hence, an assessment of the quality of historical data based on reliability of the method alone is virtually impossible. Many important earlier studies did not collect certain quality assurance information now shown to be important in field monitoring (Von Lehmden and Nelson, 1977). In other cases, supporting data were collected, but are no longer available. Therefore, critical assessment of the methodology will focus on those areas that are the most important to the general usefulness of the method, except in cases where specific problems of a selected study were quantified in the open literature.

3.2 MEASUREMENT TECHNIQUES FOR SULFUR DIOXIDE

3.2.1 Introduction

Atmospheric SO_x originates from both natural and manmade sources. Sulfur dioxide (SO_2) is the predominant SO_x in the atmosphere. This section discusses commonly used techniques for determining atmospheric concentrations of SO_2.

Manual methods for determination of SO_2 are those in which sample collection, preparation, and analysis, or some combination thereof, are performed by hand. Automated methods are those in which sample collection and analysis are performed continuously and automatically by devices generally referred to as continuous analyzers.

This section briefly describes each method, emphasizing measurement principle and method characteristics, such as detection limits and interferences. Sample collection and method calibration are discussed for both manual and automated methods. The most widely used manual methods are discussed first. Sulfation methods are presented last because they measure "sulfation rate" rather than ambient SO_2 concentration per se. The discussion of automated methods follows a semichronological order, with earlier continuous analyzers described first. Much of the descriptive information in the section is based on a review by Tanner et al. (1978). Also discussed in this section are various continuous analyzers designated by EPA as equivalent methods for the measurement of atmospheric SO_2 to determine compliance with National Ambient Air Quality Standards (NAAQS).

3.2.2 Manual Methods

3.2.2.1 Sample Collection--A number of methods use aqueous solutions for collection of SO_2. The efficiency of mass transfer of SO_2 from air to the solution phase depends on the gas-liquid contact time, diffusion coefficients of SO_2 in the gas and liquid phases, bubble size, concentration of SO_2, and solubility of SO_2 in solution. Calvert and Workman (1960) describe a method to predict the efficiency of various bubbler designs in collecting SO_2. Their method is predominantly qualitative, but it can serve as a useful guide. The most efficient designs include that of Wartburg et al. (1969); the Greenberg-Smith impinger (Smith et al., 1961); midget impingers (Jacobs et al., 1957); Drechsel bottles (British Standards Institution, 1963); and packed columns (Bostrom, 1966), which are useful where low flow rates are involved. In using such devices, care must be taken to prevent carryover of solution at high flow rates and to compensate for solvent losses by evaporation.

Collection efficiency depends in part on the solution in which SO_2 is actively dissolved and stabilized. One current method involves stabilization of SO_2 as the sulfite anion in an aqueous solution of sodium or potassium tetrachloromercurate, with which the sulfite anion complexes. To prevent conversion of sulfite to sulfate, the temperature of the collecting solution must be maintained below 20°C. Failure to maintain temperature control of samples during collection, shipment, and storage leads to underestimation of SO_2 levels in the atmosphere, particularly during summer months. Another approach involves collection in aqueous solution and conversion to the sulfate anion by oxidizing agents such as H_2O_2. Although stabilization of SO_2 as the sulfate anion can be effective, some of the soluble sulfate in the atmospheric aerosol is collected (unless removed by a particle filter) and added to the sample; thus, discrimination between SO_2 and sulfate may be impossible.

Several methods employ alkaline solutions for the absorption of SO_2. Although their collection efficiency is quite high, alkaline solutions rapidly oxidize the collected sulfite anion to sulfate unless some means are available for the direct complexation and stabilization of the sulfite anion.

Another collection technique uses filter papers or tapes impregnated with an alkaline reagent such as potassium hydroxide, triethanolamine, or potassium carbonate, together with small amounts of glycerol as an humectant (Lodge et al., 1963; Huygen, 1963; Pate et al., 1963; Forrest and Newman, 1973). The collected SO_2 is supposed to be maintained as a sulfite, but it may be oxidized to sulfate. Although laboratory tests have shown that such oxidation can be negligible, field tests have produced very erratic results. Typical PM contains traces of transition metal ions, which promote rapid oxidation of sulfite to sulfate. Prefilters should be used to eliminate PM. Oxidation of the collected sulfite to sulfate prior to analysis is also recommended. As an alternative, an analytical technique that measures the sum of sulfite and sulfate may be employed.

Some of the earlier methods for estimating ambient SO_2 concentrations (sulfation methods) are based on the reaction of SO_2 with lead dioxide to form lead sulfate (Wilsdon and McConnell, 1934). The SO_2 is stabilized in the form of a sulfate, eliminating the problem of oxidative conversion; however, any particulate matter containing sulfate species that comes into contact with the collection surface will lead to errors.

Occasionally, samples of ambient air are collected in a gas-tight syringe or other suitable container for later analysis. The reactivity of SO_2 is a major problem, however. Natusch et al. (1978) have reported extensive adsorption losses of SO_2 on thick-walled Mylar® laminates, Tygon®, Teflon®, and stainless steel container walls.

3.2.2.2 Calibration--The relationship between true pollutant concentration and the measured value by any method is determined by calibration. For methods that measure relative exposure to sulfur species (e.g., sulfation methods), no calibration is usually attempted. With these methods, use of uniform reagents, equipment, and procedures is essential to compare exposure data over time and space. Methods involving direct collection of air samples for later analysis or collection of the SO_2 in an air sample by absorption or adsorption require calibration of both the sample volume measurement and the analytical measurement.

Devices used for sample volume measurement generally are calibrated against reliable volume standards. The analytical measurement often is calibrated statically, using a known amount of the sulfite or sulfate anion in solution. Static calibration is a rapid and simple method for checking the analytical procedure, but does not subject the overall measurement method to scrutiny since the process of SO_2 collection is circumvented. Dynamic calibration of these methods has an advantage over the static approach because it scrutinizes the total measurement, but it is time consuming and therefore not used routinely. This approach, described in more detail in Section 3.2.3 on automated methods, uses synthetic atmospheres containing the pollutant in known concentrations to define the response of the method.

3.2.2.3 Measurement Methods--This section deals with the principal manual methods for determining SO_2 in the air.

3.2.2.3.1 Colorimetric method: pararosaniline. The West-Gaeke method is probably the most widely used colorimetric procedure for SO_2 determination in ambient air (West and Gaeke, 1956). It is also the basis of the EPA reference method for measurement of SO_2 in the atmosphere (U.S. Environmental Protection Agency, 1979). In the West-Gaeke method, air is bubbled into fritted bubblers containing 0.1 M sodium tetrachloromercurate (TCM) solution, which forms a stable complex with SO_2. This complex, which resists air oxidation, was thought to be the dichlorosulfitomercurate (II) ion. Recently, however, Dasgupta and DeCesare (1981) have clearly demonstrated that the SO_3 group is bonded to mercury through the sulfur atom rather than through one of the oxygen atoms and that the complex is actually a monochlorosulfonatomercurate (II) ion. The SO_2-TCM complex is reacted with acid-bleached pararosaniline and formaldehyde to form red-purple pararosaniline methanesulfonic acid. The optical absorbance of the solution is measured spectrophotometrically at 560 nm and is, within limits, linearly proportional to the concentration of SO_2. The method is applicable to the measurement of SO_2 in ambient air using sampling periods from 30 minutes to 24 hours. The lower limit of detection of SO_2 in 10 ml of TCM absorbing solution is approximately 0.5 µg, representing a concentration of 13 µg SO_2/m^3 (0.005 ppm) in an air sample of 38.2 liters. Ozone, nitrogen dioxide, and heavy metals were negative interferents in early versions of this method.

An improved version of the West-Gaeke method was adopted by the EPA in 1971 as the reference method for determining atmospheric SO_2 (U.S. Environmental Protection Agency, 1979). Several important parameters were optimized, resulting in greater sensitivity and reproducibility, as well as adherence to Beer's Law throughout a greater working range. In the EPA method, SO_2 is collected in impingers containing 0.04 M potassium tetrachloromercurate. A 20-minute wait before analysis allows ozone, a potential interferent, to decompose. Sulfamic acid is then added, followed by a 10-minute wait, to remove interference from nitrogen oxides. Interference by heavy metals is eliminated by use of phosphoric acid in the dye reagent and the disodium salt of ethylenediaminetetraacetic acid (EDTA) in the TCM absorbing solution. The complex is then reacted with a purified pararosaniline dye reagent and formaldehyde to form the colored pararosaniline methanesulfonic acid. Absorbance is measured at 548 nm. Accuracy depends on rigid control of many critical variables: pH, temperature, reagent purity, color development time, age of solutions, and concentrations of some atmospheric interferents (Scaringelli et al., 1967). Because temperature affects rate of color formation and color fading, a constant-temperature bath is recommended for maximum precision. Highly purified reagents, especially the pararosaniline dye, are vital for acceptable reproducibility. The precision of the EPA reference method analytical procedure was estimated using standard sulfite samples (Scaringelli et al., 1967) and reported to be 4.6 percent at the 95-percent confidence level. The lower limit of detection of SO_2 in 10 ml of TCM absorbing solution was 0.75 μg, representing a concentration of 25 μg SO_2/m^3 (0.01 ppm) in an air sample of 30 liters.

A collaborative study (McCoy et al., 1973) of the 24-hour EPA reference method indicated the following: method repeatability (day-to-day variability within an individual laboratory) varies linearly with SO_2 concentration from ± 18 $\mu g/m^3$ (0.007 ppm) at concentration levels of 100 $\mu g/m^3$ (0.04 ppm) to ± 51 $\mu g/m^3$ (0.019 ppm) at concentration levels of 400 $\mu g/m^3$ (0.15 ppm); method reproducibility (day-to-day variability between two or more laboratories) varies linearly with SO_2 concentration from ± 37 $\mu g/m^3$ (0.014 ppm) at 100 $\mu g/m^3$ to ± 104 $\mu g/m^3$ (0.040 ppm) at 400 $\mu g/m^3$. The method has a concentration-dependent bias. This bias becomes significant (95-percent confidence level) at the 400 $\mu m/m^3$ level. Observed values tend to be lower than the expected SO_2 concentration level.

Results of the above collaborative study and other investigations (Blacker et al., 1973; Bromberg et al., 1974; Foster and Beatty, 1974) suggest that pararosaniline methods tend to underestimate SO_2 concentrations by 5 to 20 percent. In the Bromberg study, simulated 24-hour bubbler samples were analyzed by 134 laboratories throughout the United States. Observed negative biases ranged from -3 percent for a 45 $\mu g/m^3$ sample to -16 percent for a 767 $\mu g/m^3$ sample, but reasons for the negative biases have not been determined. Based on the Bromberg study results, EPA recommended that intralaboratory quality control programs be upgraded and improved in laboratories that routinely analyze SO_2-TCM samples. EPA also recognized the need for and promoted development of standard reference samples for use in laboratory quality control programs.

More recent information, on the reliability of pararosaniline analytical procedures has been obtained through EPA's ambient air audit program. In this program, freeze-dried mixtures of sodium sulfite and TCM are sent to participating laboratories for analysis. These simulated field samples represent ambient SO_2 concentrations ranging from about 10 to 200 $\mu g/m^3$ (0.004 to 0.076 ppm). EPA audit results from 1976-1978 summarized by Bromberg et al. (1979, 1980) indicate no apparent problems with bias (accuracy) in the analytical portion of the pararosaniline methods.

Subsequent to promulgation of the SO_2 reference method, effects of temperature on the method have been studied (Kasten-Schraufnagel et al., 1975; Sweitzer, 1975). Fuerst et al. (1976) showed that collected SO_2-TCM samples decay at a temperature-dependent rate. Table 3-1 indicates that sample collection at 25°C results in a 1.1 percent loss in SO_2 during the 24-hour sampling period, but further exposure of the collected sample for 4 days at this temperature leads to a 10 percent loss in SO_2. Significant decay can occur during collection of ambient samples and during shipment and storage of collected samples when TCM solutions are exposed to temperatures above 20°C. Under typical field conditions, temperature exposure is quite often extreme, especially during the summer months at sites with relatively little protection from the elements (e.g., rooftops).

TABLE 3-1. TEMPERATURE EFFECT ON COLLECTED SO_2-TCM SAMPLES
(EPA REFERENCE METHOD)

		Percent SO_2 remaining			
		At end of sampling	Days of Exposure		
°C	°F		2	4	6
15	59	99.8	99.0	98.2	97.4
20	68	99.6	97.8	96.1	94.3
25	77	98.9	94.4	90.2	86.1
30	86	97.4	87.4	78.5	70.4
35	95	95.1	74.1	57.9	45.2
40	104	87.6	50.8	29.5	17.2

Source: Fuerst et al. (1976).

Measures to minimize these temperature effects have been investigated by Martin (1977), who recommends use of thermostatted shelters to house sampling equipment during sample collection. The temperature of samples during shipment can be controlled with cold-pack shipping containers. When samples are stored before being analyzed, refrigeration at 5°C minimizes further decay. Temperature control procedures are currently being incorporated in the EPA reference method.

A variation of the pararosaniline method that eliminates the use of the toxic mercuric chloride has recently been reported (Dasgupta et al., 1980). In this method a dilute solution of formaldehyde, buffered at pH 4 with potassium hydrogen phthalate, is used to collect and stabilize atmospheric SO_2 as hydroxymethanesulfonic acid. Sulfite, liberated from the compound by base, is added to acidic pararosaniline for color development. The optical absorbance of the colored solution is measured at 580 nm. The method is comparable to the established pararosaniline methods in absorption and recovery efficiency, sensitivity, and precision. No unusual interferences are observed due to O_3, NO_2, and transition metal ions, except Mn (II). The stability of collected SO_2 samples is significantly greater than that observed for samples collected in TCM. The reported decay rates are 0.033 percent/day and 0.3 percent/ day at room temperature and 37°C respectively. No photochemical degradation of collected samples was observed after 8 hours of exposure to bright sunlight.

Under the provisions of EPA's "Ambient Air Monitoring Reference and Equivalent Methods" regulations (U.S. Environmental Protection Agency, 1979b), two additional pararosaniline methods have been designated as equivalent methods (U.S. Environmental Protection Agency, 1975). These methods are identified as:

1. EQS-0775-001, "Pararosaniline Method for the Determination of Sulfur Dioxide in the Atmosphere - Technicon I Automated Analysis System."
2. EQS-0775-002, "Pararosaniline Method for the Determination of Sulfur Dioxide in the Atmosphere - Technicon II Automated Analysis System."

These methods employ the same sample collection procedure used in the EPA reference method and an automated analytical measurement based on the colorimetric pararosaniline method.

3.2.2.3.2 Titrimetric method: hydrogen peroxide. The British Standard Method uses a single-day or 7-day sampling instrument for the measurement of smoke and SO_2 (British Standards Institution, 1963). Air is drawn through a filter paper and into a Drechsel bottle containing ~0.3 percent hydrogen peroxide solution adjusted to pH 4.5. The H_2O_2 oxidizes the atmospheric SO_2 to H_2SO_4, which is subsequently titrated with standard sodium borate using the mixed indicator of the British Drug House (gray at pH 4.5). The method is capable of measuring SO_2 concentrations from about 25 to 25,000 $\mu g/m^3$ (0.01 to 10 ppm) using a 24-hour sampling period.

Since the method measures total acidity rather than SO_2 specifically, any strong acids that are collected produce positive errors. Normally the concentration of such substances is low relative to that of SO_2, and the measurement is generally accepted as a good approximation of the actual SO_2 concentration. Ammonia will neutralize the H_2SO_4 and give negative errors. When the presence of ammonia is suspected, a portion of the absorbing solution can be analyzed for dissolved ammonia and the SO_2 measurement adjusted accordingly.

An instruction manual on the use of the hydrogen peroxide method in the British National Survey was issued in 1966 (Warren Spring Laboratory, 1966). The manual discusses the quality of the water used for reagent preparation and states that it need not be free of carbon dioxide. Martin and Barber (1971), however, reported that use of water rich in carbon dioxide can lead to significant negative errors in the method. During sample collection and subsequent standing, sufficient carbon dioxide can be evolved from the absorbing solution to cause low titers and, on some occasions, to result even in alkaline solutions. The instruction manual also discusses the problem of alkaline contamination in the glassware required in the method. The Drechsel bottles used during sample collection and sample storage bottles need to be conditioned with absorbing reagent prior to use. Likewise, alkaline contamination in other glass parts of the sampling apparatus can lead to underestimation of ambient SO_2 levels.

Evaporation of absorbing reagent during sampling can result in overestimation of ambient SO_2 levels with the hydorogen peroxide method (Fry, 1970). If evaporation occurs, the pH of the solution is lowered and a portion of the standard alkali added during the subsequent titration is required to compensate for this effect alone. The effect is likely to be more prevalent in the summer months and can lead to overestimation of SO_2 levels by up to about 15 $\mu g/m^3$ (0.006 ppm). Fry reports that this source of error can be overcome either by making up the absorbing solution to its original volume prior to the titration or by making a mathematical correction to the titration result based on the final volume of absorbing solution after collection.

Uncertainty in the titration endpoint and rounding-off of the volume of alkali required in the titration to the nearest 0.1 ml each introduce errors of up to about ±5 μg/m^3 (0.002 ppm) (Warren Spring Laboratory, 1975). Other potential sources of error in the method include inaccurate air sample volume measurements and conversion of ambient SO_2 to sulfate on the smoke filter used in the sampler.

Warren Spring Laboratory (1962) has reported the reproducibility of the hydrogen peroxide method, based on results from five comparative studies using duplicate sampling apparatus. The coefficients of variation were on the order of 15 to 20 percent for SO_2 concentrations ranging from about 15 to 250 μg/m^3 (0.006 to 0.095 ppm) and 5 to 10 percent for concentrations ranging from about 100 to 800 μg/m^3 (0.033 to 0.305 ppm). The same reagents and analytical apparatus were used to service all the samplers in each study, thus obviating a further potential source of error.

In a more recent investigation (Barnes, 1973), duplicate SO_2 measurements were obtained with the British Standard Method at a residential site where ambient levels were low (18 to 84 μg/m^3) (0.007 to 0.032 ppm). Nineteen sets of observations were made from two samplers with a common inlet using the same supply of reagents and glassware and a further 18 sets of observations were made using a separate supply for each. Differences in measured concentrations using the two samplers on individual occasions ranged up to 31 percent of the mean of the two separate values. Most of these differences, however, did not exceed 13 percent of the mean. Titration error was cited as the single most common source of variation between the samplers in these experiments. An error in titration of 0.1 ml would result in an error in the measured SO_2 concentration of 7 μg/m^3 (0.003 ppm). When measuring low concentrations, such errors could represent a difference of 100 percent from the true concentration. Barnes concludes from these observations that measurement of low SO_2 concentrations with the method require great care on the part of the operator, more than might be expected of most operators.

3.2.2.3.3 Iodimetric methods. Several iodimetric methods have been used for measuring SO_2 in the atmosphere. In one version, an absorbing solution containing soluble starch, potassium iodide, dilute H_2SO_4, and standard 0.01 N iodine solution is prepared (Katz, 1950). SO_2 in the air sample reacts with this 8×10^{-5} N iodine solution to decolorize the blue iodine-starch complex. The reduction in color intensity is measured spectrophotometrically. The range of applicability is 25 to 2600 μg SO_2/m^3 (0.01 to 1 ppm), depending upon the volume and concentration of absorbent solution and the volume of air sampled. In a modification of this method, the excess iodine is titrated with a standard thiosulfate solution (Katz, 1969).

Oxidizing gases interfere to give low results; reducing agents interfere to give high results. Interference from high concentrations of nitrogen oxides or O_3 can be removed by introducing hydrogen into the air sample and passing the mixture over a platinum catalyst at 100°C (Bokhaven and Niessin, 1966).

In another version, air is bubbled through a sodium hydroxide solution that absorbs SO_2 (Jacobs, 1960). After acidification of the solution, the liberated sulfurous acid is titrated with standard iodine solution, using starch as an indicator. Because sulfite oxidizes to sulfate in the alkaline absorbent solution, samples cannot be stored. Oxidizing agents, NO_2, and O_3 interfere, resulting in an underestimation of the SO_2 concentration. Hydrogen sulfide (H_2S) and other reducing agents result in an overestimation. For an 850-liter air sample collected at 30 liters/minute, the lower limit of detection is 25 μg SO_2/m^3 (0.01 ppm) (Terraglio and Manganelli, 1962).

3.2.2.3.4 Impregnated filter paper methods. Filter papers, impregnated with alkali plus a humectant to keep them moist, will absorb SO_2 from air samples (Lodge et al., 1963; Huygen, 1963; Pate et al., 1963; Forrest and Newman, 1973). Two solutions commonly used to impregnate papers are a mixture of 20 percent potassium hydroxide and 10 percent triethanolamine, and a mixture of 20 percent potassium carbonate and 10 percent glycerol. The treated filters are inserted into filter holders, and air is aspirated through them. An untreated prefilter is generally recommended to remove particulate matter. Absorbed SO_2 can be extracted from the papers and determined colorimetrically by the West-Gaeke method. The alkali must be neutralized exactly to attain the proper acidity prior to color development. Alternatively, the extract solution may be treated with an oxidizing agent, such as H_2O_2 to convert sulfite to sulfate, followed by a sulfate analysis (Johnson and Atkins, 1975; Forrest and Newman, 1973).

Efficiency of SO_2 absorption is better than 95 percent under average weather conditions but decreases rapidly below 25-percent RH and above 80-percent RH. The error may be minimized by using two filter papers in series (Forrest and Newman, 1973). Elimination of glassware and reagents during sampling removes the possibility of spillage or breakage during transport. Sampled papers may be stored conveniently for long periods before being analyzed.

Sulfur dioxide SO_2 may be sampled on Whatman No. 17 filter papers impregnated with tetrachloromercurate TCM solution containing mercuric chloride, sodium chloride, ethyl alcohol, and glycerol in water (Axelrod and Hansen, 1975). Sampled filters are extracted with TCM, and the West-Gaeke procedure generally follows. Capacity of the 47-mm filters is 13 mg of SO_2, after which collection efficiency decreases. Samples collected at very low RH (10 percent) cannot be stored more than 1 day before exhibiting losses. Filters sampled at 40 percent RH may be safely stored for 1 week. No interference is observed for NO_2 and H_2S, but O_3 at 175 μg/m^3 (0.09 ppm) causes negative errors.

A method that uses nondispersive X-ray fluorescence to measure ambient SO_2 collected on sodium carbonate-impregnated membrane filters has been developed by Hardin and Shleien (1971). After collection, the sample filter is irradiated with a one millicurie iron-55 source. The resulting 2.3 kev sulfur X-rays are counted by a proportional counter with a beryllium window. A minimum detectable quantity of 30 μg SO_2 can be detected by the counter, equivalent to 25 μg/m^3 (0.01 ppm) using a collection time of 1 hour and a sampling rate of 20 liters/minute. Chlorine gas is collected to a significant degree and since its characteristic X-ray cannot be distinguished from that of sulfur, it may interfere to produce elevated results if not removed prior to encountering the treated filter.

3.2.2.3.5 Chemiluminescence method. The basis for this method is the chemiluminescence produced when a sulfite solution is oxidized (Stauff and Jaeschke, 1975). Ambient SO_2 is absorbed in 50 ml of tetrachloromercurate solution to form the monochlorosulfonatomercurate ion. Five milliliters of 2×10^{-5} N $KMnO_4$ in 10^{-3} N H_2SO_4 is added. Oxidation of the absorbed sulfite is accompanied by a chemiluminescence, which is detected by a photomultiplier tube. The total light yield, measured by a photon counting system, is proportional to the oxidizable sulfite. By sampling 1 m^3 of air, 0.5 $\mu g/m^3$ (0.2 ppb) of SO_2 may be detected with an error of less than 10 percent.

3.2.2.3.6 Ion exchange chromatographic method. Small et al. (1975) have described an ion exchange chromatographic system that separates ionic species and effectively neutralizes the eluant, allowing a conductometric measurement of the ion. A commercial instrument based on the above system is now available (Dionex Corporation, 1975) for use in trace anion analysis. In this system, a strong base anion exchanger of low capacity, agglomerated onto a surface-sulfonated DVB resin, is used as the analytical column. This is followed by a high capacity, strong acid exchange column that converts the eluant (typically 0.003 M Na_2CO_3 + 0.024 M $NaHCO_3$) into a nonconducting carbonic acid solution, after which the separated ions are monitored with a high sensitivity, multirange conductivity meter. Although the method is not totally free from ambiguity, careful selection of eluant and ion chromatographic exclusion steps can effectively separate ionic species of interest.

Mulik et al. (1978) have developed a method for collection and ion exchange chromatographic analysis of atmospheric SO_2. The method uses dilute (0.6 percent) H_2O_2 to collect the ambient SO_2. The resultant sulfate ion is analyzed by ion exchange chromatography. When a prefilter is used in the sampling train to remove aerosol sulfates, there are no apparent interferences. Collection efficiency is approximately 100 percent over the range of the method, 25 to 1300 µg SO_2 /m^3 (0.01 to 0.5 ppm).

A novel approach for the ion chromatographic determination of atmospheric SO_2 has recently been suggested by Dasgupta (1981). Sulfur dioxide is collected and stabilized as hydroxymethanesulfonic acid in a dilute solution of formaldehyde buffered at pH 4 with potassium acid phthalate (KHP). The sample is analyzed by an ion chromatographic procedure using KHP as the eluant. The hydroxymethanesulfonate ion elutes as a very sharp peak and the analysis is facilitated by the fact that both the sample and the eluant have the same ionic background of KHP, thus minimizing any undesirable phthalate peak or solvent dip.

3.2.2.3.7 Sulfation methods. Sulfation methods are based on the reaction of gaseous SO_2 in air with lead dioxide (PbO_2) paste to form lead sulfate ($PbSO_4$). They are cumulative methods for estimating average concentrations over extended periods. In the lead dioxide gauge method (Department of Scientific and Industrial Research, 1933) and the lead candle method (Wilsdon and McConnell, 1934), the paste is prepared by mixing PbO_2, gum tragacanth, alcohol, and water. The paste is applied to a piece of cotton gauze wrapped around a cylinder 10 cm in circumference and 10 cm high. After drying, the cylinder is exposed to the atmosphere in a sheltered location. After exposure, the gauge and sulfated lead dioxide are treated with sodium carbonate solution, and the dissolved sulfate is then determined gravimetrically or turbidimetrically. Measurements with the method are reported as sulfation rates (mg SO_3/100 cm^2/day). In the sulfation plate method (Huey, 1968), a similar paste containing glass filter fibers is poured into a plastic petri dish 48 mm in diameter. After drying, the plate is exposed to the atmosphere and analyzed for sulfate.

Sulfation methods have the advantage of being inexpensive, but their accuracy is subject to many physical and chemical variables and interferents. For example, the rate of sulfate formation is proportional to atmospheric SO_2 concentration up to 15-percent conversion of the lead dioxide (Wilsdon and McConnell, 1934). Reaction rate increases with temperature and with humidity. Other factors affecting rate of sulfation are purity of the lead dioxide, its particle size and shape, wind velocity, and shape of the shelter (Bowden, 1964). Positive errors are contributed by hydrogen sulfide and sulfate aerosols. Methyl mercaptan is a potential negative interferent.

Huey et al. (1969) compared the sulfation plate method with the sulfation candle method at some 250 sampling sites nationwide. A correlation coefficient of 0.95 was obtained, confirming that both methods are measuring the same species. The results also indicated that sulfation plates are 10-percent less reactive than sulfation candles.

Various attempts have been made to correlate sulfation methods with more specific methods for estimation of SO_2 concentrations. In 1962, as part of the establishment of the British National Survey, measurements with the lead dioxide gauge were compared to simultaneous measurements with the hydrogen peroxide method (Warren Spring Laboratory, 1967). The correlation between 829 pairs of results from 20 sites over 4 years was highly significant, showing that both methods were predominantly affected by the same pollutant, SO_2. The Warren Spring Laboratory concluded, however, that there was no generally applicable conversion factor for relating lead dioxide and hydrogen peroxide results. The conversion from lead dioxide to hydrogen peroxide reading was not recommended except to give a rough indication of the levels of concentration concerned.

Stalker et al. (1963) compared the lead dioxide method and the pararosaniline method to measure SO_2 at 123 stations in Nashville, Tennessee. The lead dioxide method was considered good for estimating mean SO_2 levels in communities during months with arithmetic mean concentrations of at least 65 $\mu g/m^3$ (0.025 ppm). The reliability of these mean estimates was estimated to be within ± 25 percent. Seasonal effects were noted, however, and the lead peroxide estimates of SO_2 (using an average factor of 0.031 for conversion of sulfation rate in mg SO_3/100 cm^2/day to SO_2 concentration in ppm) during the spring season of low SO_2 levels were about twice as high as simultaneous 24-hour colorimetric measurements of SO_2.

Huey et al. (1969) compared ambient SO_2 measurements by conductometric, coulometric, and colorimetric methods with sulfation results. They concluded that sulfation data in mg SO_3/100 cm^2/day could be converted to SO_2 concentrations in ppm by multiplying by 0.03. They also determined that 95 percent of the time this approximation from a single sulfation value will lie within a factor of about 3 of any single measurement using the other techniques.

3.2.2.3.8 Other manual methods. Other manual methods that have been used for the measurement of ambient concentrations of SO_2 include the barium perchlorate-thorin titrimetric method (Fritz and Yamamura, 1955), the barium sulfate turbidimetric method (Volmer and Frohlich, 1944), the barium chloranilate colorimetric method (Bertolacini and Barney, 1957), and the silica gel reduction method (Stratmann, 1954).

3.2.3 Automated Methods

3.2.3.1 Sample Collection--In continuous SO_2 analyzers, sample collection is an integral part of the total automated measurement process. The sample line leading from the sample manifold to the inlet of the analyzer should be constructed of an inert material such as Teflon®. The sample line dimensions (length and internal diameter) should be selected to minimize the residence time without creating a significant pressure drop between the sample manifold and the analyzer inlet. The use of an inert particle filter at the inlet of the analyzer should depend on the analyzer's susceptibility to interference, malfunction, or damage due to PM. Heavy loading of PM on the filter may lead to erroneous SO_2 measurements; therefore, it may be necessary to change the filter frequently.

3.2.3.2 Calibration--The relationship between true pollutant concentration and the response of a continuous analyzer is best determined by dynamic calibration. In dynamic calibration, zero air and standard atmospheres containing known concentrations of SO_2 are introduced into the analyzer to define the analyzer response over the full measurement range. Dynamic calibration provides evidence that all components of the instrument are functioning properly.

Standard atmospheres required for calibration purposes may be generated using permeation tubes (O'Keeffe and Ortman, 1966), (i.e., sealed Teflon® tubes containing liquified gas). Gas diffuses through the walls at a low, constant rate at constant temperature. The gas is then diluted with zero air at accurately known flowrates to obtain SO_2 concentrations over the required range. Permeation tubes with certified permeation rates are available from the National Bureau of Standards (NBS) as Standard Reference Materials (SRM's) or from commercial suppliers. Dynamic calibration may also be carried out using known concentrations of SO_2 in high-pressure cylinders. To ensure stability, they are usually prepared in high concentrations and dynamically diluted to the desired level. Traceability of such standards to NBS SRM's may be established by the gas standard manufacturer or by the user.

Static calibration techniques are possible for several of the continuous SO_2 analyzers described below. Static calibration introduces a stimulus to measure instrumental response under no sample air flow conditions. Typical stimuli are electrical signals, solutions chemically equivalent to the pollutant, or solutions producing comparable physical effects upon properties by which the pollutant is detected, such as optical density or electrical conductivity. Static calibration is a rapid and simple method for checking various components of the instrument, but does not scrutinize total instrument performance.

3.2.3.3 Measurement Methods--The principal automated methods (continuous analyzers) for determining SO_2 in the air are discussed in this section in chronological order.

3.2.3.3.1 Conductometric analyzers. Conductometric analyzers were the first commercially available instruments for continuously monitoring atmospheric SO_2. They are still used today. In their operation, air is brought into contact with an absorbing solution, which dissolves SO_2. The ions formed by SO_2 dissolution increase the conductivity, which is proportional to the concentration. The absorbent may be either deionized water or acidified hydrogen peroxide solution. When water is used, conductance is increased by formation of the sulfite and bisulfite ions:

$$SO_2 + H_2O \rightleftarrows SO_2 \cdot H_2O \rightleftarrows H^+ + HSO_3^- \qquad (3\text{-}1)$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^{-2}$$

Hydrogen peroxide solution oxidizes SO_2 to form sulfuric acid:

$$SO_2 + H_2O_2 \rightarrow H_2SO_4 \rightleftarrows H^+ + HSO_4^- \qquad (3\text{-}2)$$

$$HSO_4^- \rightleftarrows H^+ + SO_4^{-2}$$

Conductance is measured by a pair of inert (platinum) electrodes within the cell. To increase accuracy, comparison is made to a reference cell, which measures conductance of unused absorbent. The response characteristics of conductometric analyzers include lower detection limits ranging from 0.005 to 0.04 ppm (10 to 100 $\mu m/m^3$), lag times (time interval from change in input concentration to change in output signal) ranging from 5 to 200 seconds, and response times (time interval from change in input concentration to 90 percent of maximum output signal) ranging from 1 to 4 minutes (Lawrence Berkeley Laboratory, 1972).

The major disadvantage of conductometric analyzers is their susceptibility to interference by any species that either forms or removes ions from solution and changes the conductivity of the solution. The degree of interference depends on humidity, temperature, SO_2 concentration, and the particular instrument. The worst interferents are chlorine, hydrochloric acid, and ammonia (Rodes et al., 1969); nitrogen dioxide and carbon dioxide interfere to a lesser extent. Airborne particles, especially oceanborne salt aerosols, are potentially damaging. Several methods have been used to minimize these problems. Chemical scrubbers, which selectively remove gaseous interferents, have been incorporated into some conductometric analyzers. Particle filters have also been employed.

3.2.3.3.2 Colorimetric analyzers. Colorimetric analyzers are based upon reaction of SO_2 with solutions of organic dyes to form colored species. Optical absorbance of the resulting solution, measured spectrophotometrically, is within limits linearly proportional to the concentration of the colored species in accordance with Beer's Law. Most instruments use modified versions of the manual pararosaniline method developed by West and Gaeke (1956). Automation of the West-Gaeke method per se does not ensure a practical continuous monitoring instrument since some solutions require daily preparation.

The response characteristics for some commercially available instruments include lower detection limits ranging from 0.002 to 0.01 ppm (5 to 25 $\mu m/m^3$), lag times ranging from 0.6 to 25 minutes, and response times ranging from 5 to 30 minutes (Lawrence Berkeley Laboratory, 1972). Advantages of these instruments include good sensitivity and, with proper control, good specificity. Interferences by nitrogen oxides may be controlled by using a reagent containing sulfamic acid. Heavy metals may be complexed with EDTA in the scrubbing solution or with phosphoric acid in the dye solution. Ozone interference may be controlled by use of a delay coil downstream from the absorber to allow time for ozone to decay, but this results in longer lag and response times. Major disadvantages of these instruments are the need for reagent and pump tubing replacement and frequent recalibration.

3.2.3.3.3 Coulometric and amperometric analyzers. Coulometric analyzers are based on the reaction of SO_2 with a halogen, formed directly by electrolysis of a halide solution. The current necessary to replace the depleted halogen is proportional to the amount of SO_2 absorbed in the solution, and hence to the SO_2 concentration in the air.

In one common coulometric system, an inner chamber, into which air is introduced, is contiguous with an outer chamber (Treon and Crutchfield, 1942). Both contain a solution of potassium bromide and bromine in dilute sulfuric acid. Potential difference between chambers, relative to a reference potential, is measured by the reference electrodes. As absorbed SO_2 reduces the Br_2 concentration in the inner chamber, the amplifier produces a current to restore the Br_2 content in the inner chamber until the potential difference is again zero. In a second system, the change in halogen concentration is detected as a current change rather than a potential difference. The cell is filled with a potassium iodide solution, buffered to pH 7. At the platinum anode, a constant current source continuously generates iodine, which is subsequently reduced at the cathode. An equilibrium concentration of iodine is established, and no current is generated at an activated-carbon bipolar reference electrode, connected in parallel. Reaction with SO_2 decreases the equilibrium concentration of iodine, which cannot transport the charge generated by the constant-current source. Part of the current is diverted through the reference electrode; this flow is proportional to the SO_2 concentration in the air sample. The response characteristics of modern coulometric analyzers include lower detection limits ranging from 0.002 to 0.05 ppm (5 to 130 $\mu m/m^3$), lag times ranging from 2 to 120 seconds, and response times ranging from 2 to 5 minutes (Lawrence Berkeley Laboratory, 1972).

Interferent species are those able to oxidize halides, reduce halogens, or complex with either. They consist primarily of sulfur compounds (hydrogen sulfide, mercaptans, and organic sulfides and disulfides) with sensitivities comparable to or greater than that of SO_2. Other potential interferents, at lower sensitivities, are ozone, nitrogen oxides, chlorine, olefinic hydrocarbons, aldehydes, benzene, chloroform, other nitrogen- or halogen-containing compounds, and other hydrocarbons (DeVeer et al., 1969; Schulze, 1966; Thoen et al., 1968; Washburn and Austin, 1952). Interferences can be minimized by selective filters, which are sometimes built into the instrument or offered as optional features. For example, a heated silver gauze filter is reported to remove hydrogen sulfide, ozone, chlorine, nitrogen oxides, carbon disulfide, ethylene, aldehydes, benzene, and chloroform, but will not remove mercaptans (Philips Electronic Instruments, undated).

Minimal maintenance is the major advantage of a coulometric analyzer (reagent may need only monthly replacement; electrodes may require annual cleaning). Also, reagent consumption is negligible because of halide regeneration, and evaporated water is replaced by condensation from air or from a reservoir.

3.2.3.3.4 Flame photometric analyzers. The flame photometric detector (FPD) is based on the measurement of the band emission of excited S_2^* molecules during passage of sulfur-containing compounds through a hydrogen-rich (reducing) flame. The emitted light passes through a narrow-pass optical filter, which isolates the 394 nm S_2^* band, and is detected by a photomultiplier tube (PMT). PMT output is proportional to the square of the sulfur concentration; hence, an electronic system to "linearize" output is a desirable feature. Application of the FPD to the detection of SO_2 was first made by Crider (1965) and analyzers using FPD have been widely accepted for ambient SO_2 monitoring. The response characteristics of continuous flame photometric SO_2 analyzers include lower detection limits ranging from 0.002 to 0.010 ppm (5 to 25 $\mu m/m^3$), lag times ranging from 1 to 5 seconds, and response times ranging from 10 to 30 seconds (Lawrence Berkeley Laboratory, 1972).

Although the FPD is insensitive to nonsulfur species, it will detect sulfur compounds other than SO_2. Particle filters will remove troublesome aerosol sulfates and selective filters may be used to reduce interference from other gaseous sulfur compounds (e.g., an H_2S filter is used on most commercial instruments). Interference by CO_2 can be minimized by maintaining ambient levels of CO_2 in the calibration and sample matrices.

Gas chromatographs with flame photometric detectors (GC-FPD) are also available commercially. GC-FPD can separate individual sulfur compounds and measure them individually (Stevens et al., 1971). The temporal resolution of GC-FPD data, however, is limited by the chromatographic elution time of SO_2 and other gaseous sulfur compounds.

Disadvantages of FPD systems include the need for a source of compressed hydrogen and sensitivity to all sulfur compounds. Advantages of FPD systems include low maintenance, good sensitivity, very fast response, and good selectivity for sulfur compounds. No reagents are necessary, other than compressed hydrogen.

3.2.3.3.5 Second-derivative spectrometric analyzers. The second-derivative spectrometer processes the transmission-versus-wavelength function of a spectrum to produce a signal proportional to the second derivative of this function (Hager and Anderson, 1970). The signal amplitude is proportional to the concentration of the gas in the absorption path. These instruments center on the shape characteristics rather than basic intensity changes of molecular band spectral absorption. The slope and curvature characteristics are often large, specific, and independent of intensity. Because these shape characteristics are large but specific to individual compounds, resolution of component gases is possible.

In the operation of a second-derivative spectrometer, radiant energy from a UV or visible source is directed into a monochromator, where it is dispersed by a grating to provide monochromatic light to the sample cell. The wavelength of this light is modulated with respect to time in a sinusoidal fashion by an oscillating entrance slit. The angular position of the grating sets the center wavelength (299.5 nm) coming out of the monochromator into the multipass cell. The sample is continuously drawn through the cell by a pump. Output from the photomultiplier tube is electronically analyzed to develop the second derivative of the absorbance.

Sensitivity is enhanced because the output is an AC signal of known wavelength and phase, adaptable to high-gain electronic amplification. Uniqueness of the curvature of a given molecular band enables this type of instrument to be highly specific. A theoretical assessment by Ratzlaff and Natusch (1977) indicates that precision may be a problem with spectrometric techniques of this type. Measurements are independent of sample flowrate, but relatively high flowrates (4 liters/minute) are necessary to achieve reasonable response times. The response characteristics for one commercially available instrument include a lower detection limit of 0.01 ppm (25 $\mu m/m^3$), lag time of 1 minute, and response time of 8 minutes (U.S. Environmental Protection Agency, 1979a).

3.2.3.3.6 Fluorescence analyzers. Fluorescence analyzers are based on detection of the characteristic fluorescence released by the sulfur dioxide molecule when it is irradiated by ultraviolet light (Okabe et al., 1973). This fluorescent light is also in the ultraviolet region of the spectrum, but at a different wavelength than the incident radiation. Wavelengths between 190 and 230 nm are used for excitation and the fluorescent wavelengths usually monitored are between 300 and 400 nm. In this region of the spectrum, there is relatively little quenching of the fluorescence by other molecules occurring in ambient air. The light is detected by a photomultiplier tube that, through the use of electronics, produces a voltage proportional to the light intensity and SO_2 concentration. The fluorescent light reaching the photomultiplier tube is usually modulated to facilitate the high degree of amplification necessary. Some analyzers mechanically "chop" the incident irradiation before it enters the sample cell. Other instruments electronically pulse the incident light source at a constant rate. The response characteristics of fluorescence analyzers include lower detection limits of 0.005 ppm, lag times of about 30 seconds, and response times of about 5 minutes (U.S. Environmental Protection Agency, 1979a).

Potential interferences to the fluorescence technique include any species that either quenches or exhibits fluorescence. Both water vapor and oxygen strongly quench the fluorescence of SO_2 at some wavelengths. Water vapor can be removed by a dryer within the instrument or the water interference can be minimized by careful selection of the incident radiation wavelength. The effect of oxygen quenching can be minimized by maintaining identical oxygen concentrations in the calibration and sample matrices.

Aromatic hydrocarbons such as naphthalene exhibit strong fluorescence in the same spectral regions as SO_2 and are major interferents. These aromatics must be removed from the sample gas stream by an appropriate scrubber upstream of the sample cell. The scrubbers may operate at ambient or elevated temperature. Certain elevated-temperature scrubbers, however, have the potential for converting ambient H_2S (which normally does not interfere with the fluorescence technique) into SO_2. In these cases, the hydrocarbon scrubber must be preceded by a scrubber for H_2S.

3.2.3.3.7 Other automated methods. Other automated methods (continuous analyzers) that have been used for the measurement of ambient concentrations of SO_2 include: voltammetry (Chand and Marcote, 1971); correlation spectroscopy (Barringer Research, Ltd., 1969; Moffat et al., 1971); and differential lidar (Johnson et al., 1973).

3.2.3.4 EPA Designated Equivalent Methods--Under provisions of EPA's "Ambient Air Monitoring Reference and Equivalent Methods" regulations (U.S. Environmental Protection Agency, 1979b), several commercial continuous analyzers have been designated as equivalent methods for determining compliance with National Ambient Air Quality Standards for SO_2. These analyzers have undergone the required testing and meet EPA's performance specifications for automated methods, summarized in Table 3-2. A list of SO_2 analyzers designated from the promulgation of the regulations in 1975 to December 31, 1980, is given in Table 3-3. Information on designation of these analyzers as equivalent methods may be obtained by writing the Environmental Monitoring Systems Laboratory, Methods Standardization Branch (MD-77), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

Review of performance data submitted in support of the designations listed in Table 3-3 indicates that these modern analyzers exhibit performance better than that specified in Table 3-2. For the analyzers tested, noise levels were typically 3 ppb or less. The zero drift results (12- and 24-hour) were all less than 5 ppb and typically less than 3 ppb. The span drift results (at 20 and 80 percent of the full scale range of 0 to 0.5 ppm) were all less than 5 percent and typically 2 to 3 percent. The precision results (at 20 and 80 percent of the full scale range of 0 to 0.5 ppm) indicate a typical precision of 1 to 2 ppb. Lag times were typically less than 1 minute. Response times (rise and fall times) for the various types of analyzers were typically as follows: flame photometric, 1 minute or less; fluorescence, 5 minutes; coulometric, 3 minutes; conductometric, 0.5 minute; second-derivative spectrometric, 8 minutes. For analyzers of the same type (e.g., flame photometric), interference test results for a given potential interferent were somewhat variable. The concentration of SO_2 during the tests was 0.14 ppm and the interferent concentrations were as indicated in Table 3-4. The interference equivalent for each interferent must not exceed ±20 ppb and the total interference equivalent (sum of the absolute values of the individual interference equivalents) must not exceed 60 ppb. Interference equivalents of 5 ppb or less were obtained in each case except for the following: flame photometric-negative CO_2 interference equivalents

TABLE 3-2. PERFORMANCE SPECIFICATIONS FOR EPA EQUIVALENT METHODS FOR SO_2 (CONTINUOUS ANALYZERS)[a]

Performance parameter	Units	Specification
Range	ppm	0-0.5
Noise	ppm	0.005
Lower detectable limit	ppm	0.01
Interference equivalent		
Each interferent	ppm	±0.02
Total interferent	ppm	0.06
Zero drift, 12- and 24-hour	ppm	±0.02
Span drift, 24-hour		
20 percent of upper range limit	percent	±20.0
80 percent of upper range limit	percent	±5.0
Lag time	minutes	20
Rise time	minutes	15
Fall time	minutes	15
Precision		
20 percent of upper range limit	ppm	0.01
80 percent of upper range limit	ppm	0.015

Note: 1 ppm SO_2 = 2620 $\mu g/m^3$.

[a] Source: U.S. Environmental Protection Agency (1979b).

TABLE 3-3. LIST OF EPA DESIGNATED EQUIVALENT METHODS FOR SO_2 (CONTINUOUS ANALYZERS)

Designation number[a]	Manufacturer	Model	Measurement principle
EQSA-1275-005	Lear Siegler	SM1000	Second-derivative spectrometric
EQSA-1275-006	Meloy	SA185-2A	Flame photometric
EQSA-0276-009	Thermo Electron	43	Fluorescence
EQSA-0678-010	Philips	PW9755	Coulometric
EQSA-0876-011	Philips	PW9700	Coulometric
EQSA-0876-013	Monitor Labs	8450	Flame photometric
EQSA-0877-024	ASARCO	500,600	Conductometric
EQSA-0678-029	Beckman	953	Fluorescence
EQSA-1078-030	Bendix	8303	Flame photometric
EQSA-1078-032	Meloy	SA285E	Flame photometric
EQSA-0779-039	Monitor Labs	8850	Fluorescence
EQSA-0580-046	Meloy	SA700	Fluorescence
EQSA-1280-049	Lear Siegler	AM2020	Second-derivative spectrometric

[a] The four digits in the middle of each number indicate the month and year of designation.

TABLE 3-4. INTERFERENT TEST CONCENTRATIONS (PARTS PER MILLION)[a] USED IN THE TESTING OF EPA EQUIVALENT METHODS FOR SO_2[e]

Analyzer type[b]	Hydrochloric acid	Ammonia	Hydrogen sulfide	Sulfur dioxide	Nitrogen dioxide	Nitric oxide	Carbon dioxide	Ethylene	Ozone	m-Xylene	Water vapor	Carbon monoxide
Flame photometric (FPD)	--	--	0.1	0.14[d]	--	--	750	--	--	--	20,000[c]	50
Gas chromatography-FPD	--	--	0.1	0.14[d]	--	--	750	--	--	--	20,000[c]	50
Spectrophotometric-wet chemical (pararosaniline reaction)	0.2	0.1[c]	0.1	0.14[d]	0.5	--	750	--	0.5	--	--	--
Electrochemical	0.2	0.1[c]	0.1	0.14[d]	0.5	0.5	--	0.2	0.5	--	20,000[c]	--
Conductivity	0.2	0.1[c]	--	0.14[d]	0.5	--	750	--	--	--	--	--
Spectrophotometric-gas phase	--	--	--	0.14[d]	0.5	0.5	--	--	0.5	0.2	--	--

[a] Concentrations of interferent listed must be prepared and controlled to ± 10 percent of the stated value.

[b] Analyzer types not listed will be considered by the EPA Administrator as special cases.

[c] Do not mix with pollutant.

[d] Concentration of pollutant used for test. These pollutant concentrations must be prepared to ± 10 percent of the stated value.

[e] Source: U.S. Environmental Protection Agency (1979b).

of about 10 ppb were typical; coulometric-positive O_3 interference equivalents of about 8 ppb were typical.

As part of required equivalency testing by manufacturers, all continuous SO_2 analyzers designated by EPA as equivalent methods have demonstrated a consistent relationship with the reference method. A consistent relationship is demonstrated when the differences between (1) measurements made by the test analyzer, and (2) measurements made by the reference method are less than or equal to the allowable discrepancy specifications prescribed in the equivalency regulations, when both methods simultaneously measure SO_2 concentrations in a real atmosphere. All the equivalent methods listed in Table 3-3 have demonstrated this consistent relationship with the reference method and the observed differences between simultaneous measurements were generally well within the required specifications.

A comparison study using EPA designated equivalent methods for SO_2 was recently conducted by EPA in an urban/industrial/commercial area of Durham, North Carolina (U.S. Environmental Protection Agency, 1979a). Eight continuous SO_2 analyzers were compared over 150 days under more or less typical air monitoring conditions. During the study, the analyzers simultaneously measured ambient air sampled from a common manifold. The ambient sample was occasionally augmented with artificially generated pollutant to allow for analyzer comparisons at higher concentrations. A statistical comparison of hourly averages for each test analyzer with the average of the hourly averages (for corresponding hours) from the other test analyzers is presented in Table 3-5. Each test analyzer is identified in the table by manufacturer, model number, and measurement principle. The data clearly indicate that these continuous SO_2 analyzers are capable of excellent performance (high correlation with one another, small mean differences).

3.2.4 Summary

Methods for measuring of SO_2 can be classified as: (1) manual methods, which involve collection of the sample over a specified time period and subsequent analysis by a variety of analytical techniques, or (2) automated methods, in which sample collection and analysis are performed continuously and automatically.

In the commonly used manual methods, the techniques used for the analysis of the collected sample are based on colorimetric, titrimetric, turbidimetric, gravimetric, X-ray fluorescent, chemiluminescent, and ion exchange chromatographic measurement principles.

The most widely used manual method for the determination of atmospheric SO_2 is the pararosaniline method developed by West and Gaeke. An improved version of this colorimetric method, adopted as the EPA reference method in 1971, is capable of measuring ambient SO_2 concentrations as low as 25 $\mu g/m^3$ (0.01 ppm), with sampling times ranging from 30 minutes to 24 hours. The method has acceptable specificity for SO_2, but samples collected in tetrachloromercurate (II) are subject to a temperature-dependent decay, which can result in an underestimation of the ambient SO_2 concentration. Temperature control during sample collection, shipment, and storage effectively minimizes this decay problem. A variation of the

TABLE 3-5. COMPARISON OF EPA DESIGNATED EQUIVALENT METHODS FOR SO_2 (CONTINUOUS ANALYZERS)[b]

Analyzer	Meloy SA185-2A	Monitor Labs 8450	Meloy SA285E	Thermo Electron 43	Beckman 953	Lear Siegler SM1000	Philips PW9755	Bendix 8303
Measurement principle	Flame photometry	Flame photometry	Flame photometry	Fluorescence	Fluorescence	Second-derivative spectrometry	Coulometry	Flame photometry
Correlation coefficient[a]	0.999	0.999	0.999	0.997	0.998	0.936	0.998	0.998
Mean difference[a] ppb	-3.695	-0.006	-0.251	-0.177	5.108	4.924	5.775	-3.278
Std. dev of diff.[a] ppb	3.925	4.555	3.243	8.300	6.901	20.712	4.631	4.392
Max. abs. diff.[a] ppb	19.3	19.2	15.5	29.9	25.4	100.9	25.6	21.0
No. of abs. diff.[a] >20 ppb	0	0	0	49	21	427	13	1
No. of data pairs	3302	3186	3306	2170	1594	1820	3070	1984

[a] Between subject analyzer and average of other test analyzers (for corresponding hours).

[b] Source: U.S. Environmental Protection Agency (1979a).

Note: 1 ppb SO_2 = 2.62 μg/m^3.

pararosaniline method uses a buffered formaldehyde solution for sample collection and is reported to be less susceptible to the temperature-dependent decay problem.

In Great Britain, a titrimetric method based on collection of SO_2 in dilute H_2O_2 followed by titration of the resultant H_2SO_4 with standard alkali is the standard method and is used extensively. Although simple to perform, the method requires long sampling times (24 hours) and is subject to interference from atmospheric acids and bases. Additional sources of error with this method include evaporation of reagent during sampling, titration errors, and alkaline contamination of glassware.

Methods that collect SO_2 with alkali-impregnated filter papers for subsequent analysis as sulfite or sulfate by a variety of techniques have been developed. Most of these methods involve an extraction step prior to analysis, although nondispersive X-ray fluorescence has been used for the direct measurement of SO_2 collected on sodium carbonate-impregnated membrane filters.

Two of the most sensitive methods available use measurement principles based on chemiluminescence and ion exchange chromatography. In the chemiluminescence method, SO_2 is absorbed in a tetrachloromercurate solution and subsequently oxidized with potassium permanganate. The oxidation of the absorbed SO_2 is accompanied by a chemiluminescence that is detected by a photomultiplier tube. One method, using ion exchange chromatography to determine ambient levels of SO_2 that have been absorbed into dilute H_2O_2 and oxidized to sulfate, has been developed. Another ion chromatographic approach, using a buffered formaldehyde absorbing reagent, has been reported.

Sulfation methods, based on reaction of SO_2 with lead dioxide paste to form lead sulfate, have commonly been used to estimate ambient SO_2 concentration over extended periods. The accuracy of sulfation methods is subject to many physical and chemical variables and interferents. Sulfation rate (mg SO_3/100 cm^2/day) is commonly converted to a rough estimate of SO_2 concentration (ppm) by multiplying the sulfation rate by the factor 0.03.

Automated methods for measurement of ambient levels of SO_2 have gained widespread use in the air-monitoring community. Some of the earliest continuous SO_2 analyzers were based on conductivity and coulometry. These first-generation analyzers were subject to interference by a wide variety of substances present in typical ambient atmospheres. However, more recent commercially available analyzers using these measurement principles exhibit improved specificity for SO_2 through the incorporation of sophisticated chemical and physical scrubbers. Early continuous colorimetric analyzers using West-Gaeke type reagents and having good sensitivity and acceptable specificity for SO_2 were fraught with various mechanical problems, required frequent calibration, and never gained widespread acceptance.

Continuous SO_2 analyzers using the techniques of flame photometric detection, fluorescence, and second-derivative spectrometry have been developed over the past 10 years and are commercially available from a number of air-monitoring instrumentation companies. Flame photometric detection of ambient SO_2 is based on measurement of the band emission of excited

S_2^* molecules formed from sulfur species in a hydrogen-rich flame. The FPD analyzers exhibit high sensitivity and fast response, but must be used with selective scrubbers or coupled with gas chromatographs when high specificity is required.

Fluorescence analyzers are based on detection of the characteristic fluorescence of the SO_2 molecule when it is irradiated by UV light. These analyzers have acceptable sensitivity and response times, are insensitive to sample flowrate, and require no support gases. They are subject to interference by water vapor (due to quenching effects) and certain aromatic hydrocarbons, and therefore must incorporate some means to minimize these species or their effects.

Second-derivative spectrometry is a highly specific technique for measuring atmospheric SO_2, and continuous analyzers based on this principle are available commercially. The analyzers are insensitive to sample flowrate and require no support gases, but relatively high sample flowrates are required to achieve reasonable response times. Excessive electronic noise and inherent lack of precision can be problems with these analyzers.

Continuous analyzers based on many of the above measurement principles (conductivity, coulometry, flame photometry, fluorescence, and second-derivative spectrometry) have been designated by EPA as equivalent methods for the measurement of SO_2 in the atmosphere. Testing of these analyzers by the manufacturers prior to designation demonstrated adequate performance for use when an EPA reference or equivalent method is desired or required. EPA testing of these methods verified their performance and has also demonstrated excellent comparability among these designated methods under typical monitoring conditions.

3.3 PARTICULATE MATTER

3.3.1 Introduction

As described in Chapter 2, particulate matter (PM) suspended in ambient air presents a complex multiphase system consisting of a spectrum of aerodynamic particle sizes from below 0.01 micrometer (μm) up to 100 μm and larger. Fine particles (below ~ 2 μm) tend to remain suspended in air unless removed by external processes such as rainfall. Coarse particles (above ~ 2 μm) have appreciable settling velocities and tend to settle unless kept in suspension by high windspeeds or turbulence. The sources and characteristics of the particles in both size ranges are generally quite different, and depending on the objectives of the sampling, measurements are often made that consider only a selected size fraction. Samplers used to identify fine and coarse particle fractions typically are designed to have inlet and substage cutpoints that are as sharp as possible. Samplers used to simulate the deposition pattern of particles in the respiratory system have well-defined but more gradual cutpoints. Lippmann (1970) summarized samplers and deposition patterns in the 1-10 μm range proposed by several organizations. As Figure 3-1 shows these include models of the American Conference of Governmental Industrial Hygienists (ACGIH), British Medical Research Council (BMRC), and U.S. Atomic Energy Commission (called the "Los Alamos" curve) (Lippmann, 1970). Miller et al. (1979) proposed a sampler cutpoint of 15 μm related to respiratory system deposition but did

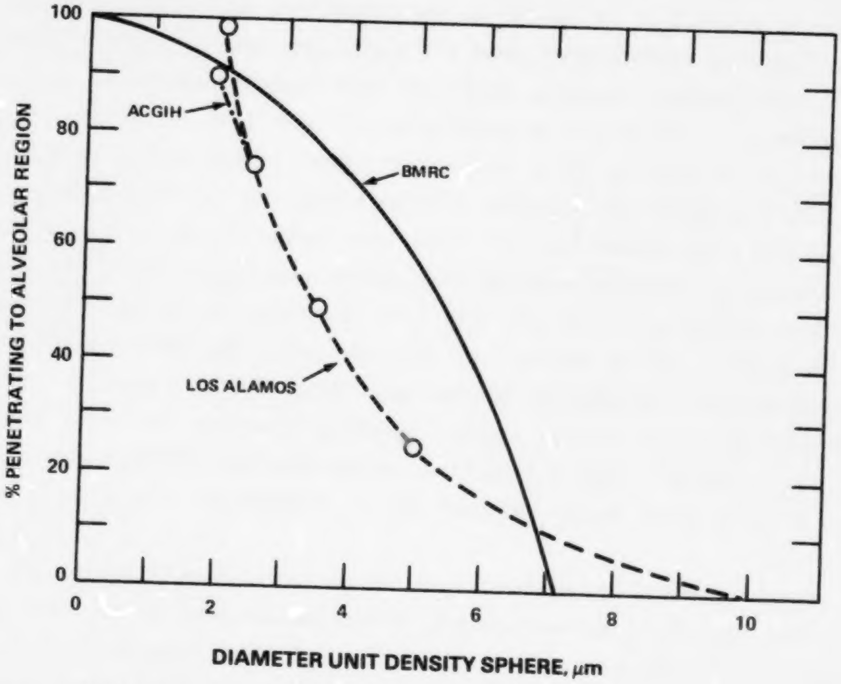

Figure 3-1. Respiratory deposition models used as patterns for sampler cutpoints.
Source: Lippmann (1970).

not recommend a desirable cutpoint sharpness. Particle deposition in the respiratory system is discussed in more detail in Chapter 11.

The aerodynamic diameter is one of the most important physical parameters when considering particle deposition in the atmosphere or the human respiratory system. Suspended particles are rarely spherical, and characterizing particle size with a single physical dimension is often difficult. Aerodynamic diameter is not a direct measurement of size but is the equivalent diameter of a spherical particle of unit density that would settle at the same rate. This definition inherently considers such factors as particle density and shape without requiring their direct measurement. Aerodynamic diameters are used in this chapter unless stated otherwise. Sampling methods using collection or separation techniques based on the inertia or settling properties of particles are classified according to the aerodynamic size. In general, all sampling methods that draw the particles into an inlet or opening perform an aerodynamic size segregation. However, particles with unusual geometries, such as long fibers may not be separated as effectively as more spherical particles, since the orientation of the fiber at the point of separation has a substantial impact on the effective diameter.

As Fuchs (1964) pointed out, particle size distributions can be examined in several ways. Separate distributions of volume, surface area, and number of particles, as shown in Figure 3-2, can be measured to provide detailed information especially useful in studying particle transport and transformation. The particle size distribution by mass is perhaps the most important characteristic of an aerosol to consider with the majority of current sampling methods. A mathematical integration of the mass distribution function over the effective aerodynamic collection range of the sampler directly provides the total mass collected per unit volume of air sampled. This information can be obtained indirectly from volume, surface area, or number distribution, but an estimate of the average particle density must be included in the calculations.

The most common aerosol measurement made in conjunction with health and welfare effect studies is the mass concentration measurement. Direct measurement of the mass concentration is made by collecting particles on a substrate, such as a filter, gravimetrically determining the mass of the particles, and dividing the mass by the volume of air sampled. Ideally, the particles reaching the substrate have been segregated by an efficient sampling mechanism that provides a defined portion of the ambient size distribution of particles to be collected. Airborne Particles (National Research Council, 1979) stated that ". . . integral methods used are always sensitive to the modification of the size distribution by the sampling inlets and transport lines used in the technique." This reference notes that Lundgren (1973), using special samplers to produce mass size distributions as shown in Figure 3-3, showed that most mass sampling methods truncate the true ambient particle distribution, thereby giving concentrations less than those actually existing. If these less-than-perfect samplers operated consistently in all conditions, the mass collected would always be a consistent proportion of the true ambient size distribution, assuming a constant distribution function.

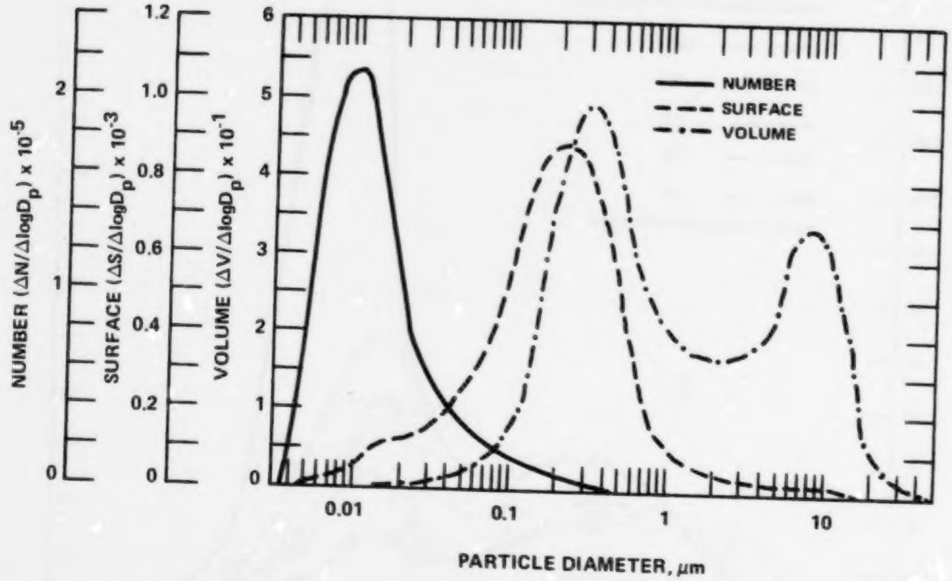

Figure 3-2. Plots illustrating the relationship of particle number, surface area, and volume distribution as a function of particle size.

Source: Whitby (1975).

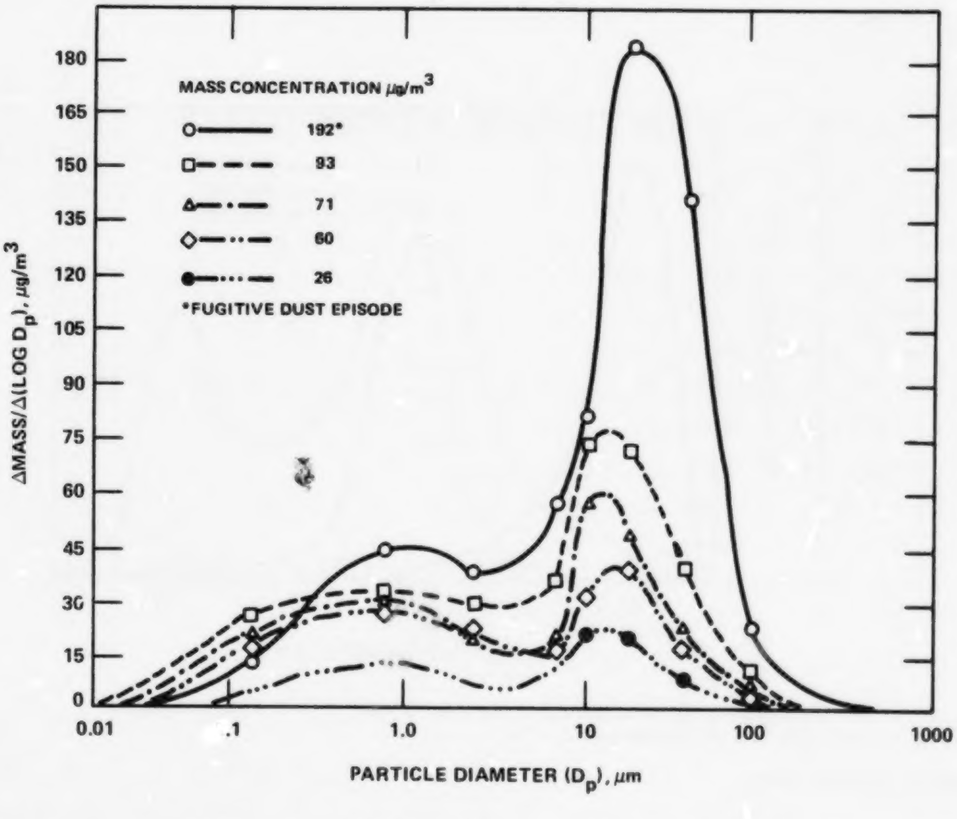

Figure 3-3. Typical ambient mass distribution data for particles up to 200 μm.

Source: Lundgren (1973).

However, it has been determined that many sampler inlets are substantially affected by windspeed and, in some cases, wind direction. Some of the commonly used PM samplers employing direct mass measurement techniques include the TSP Hi-Volume Sampler, the dichotomous sampler, cascade impactors, and cyclone samplers.

Mass concentrations of particles can be estimated using methods that do not employ direct weighing. These indirect measurements use analytical techniques other than direct weighing for assessing integral properties (other than mass) of particles. Typically, an empirical relationship with a gravimetric method is developed and pseudo-mass concentrations reported in lieu of the integral property measurement. Beta-ray attenuation by the particles on a filter and optical reflectance of the darkening of a filter by collected particles are examples of indirect measurement techniques. In situ methods, which examine particles still suspended in the airstream, include a wide variety of techniques such as the light-scattering measurements of the integrating nephelometer and the size classification capability of optical particle counters.

Analytical measurement of the chemical composition of particles can be strongly influenced by the sampling method. Surface measurements, such as X-ray fluorescence spectroscopy, require a filter that retains particles on the surface rather than allowing penetration as into a fiber filter. The composition and impurities in the collection substrate can be critical, especially in the analysis of trace elements. Selected substrates can also interact with ambient gases to produce artifact particulate matter. Section 3.3.4 contains descriptions of the most common analytical methods and Section 3.3.5. briefly discusses particle morphology measurements by microscopic examination.

Measurement technology for aerosols has advanced significantly in the past 10 years, especially in the area of size-specific measurements for larger particles. Before the advent of specially designed wind tunnels into which specific aerosol sizes and types can be injected, determination of sampling accuracy (effectiveness) under conditions similar to field sampling had rarely been attempted. For these tests, effectiveness is measured as the percent of the particle mass reaching the collection substrate of the sampler compared to results obtained by isokinetic sampling in the wind tunnel.

It has been recognized (Cermak, 1974) that the length and time scales of fluid motion in a wind tunnel can be vastly different from those existing in the atmospheric boundary layer. While ultimate agreement between the performance characteristics of an inlet for large particles tested in a wind tunnel and in the atmosphere must be substantiated, the use of a wind tunnel provides a tool to characterize inlets over a wide range of test parameters under controlled conditions. Tests conducted in the atmosphere will only provide benchmarks for comparison because of the lack of consistency of test conditions. The comparability of artificial and real particles and the turbulent macroscale on the motion of particles must be addressed when considering wind tunnel simulation. While no models exist for predicting the behavior of large particles in the atmosphere, such models are not necessarily required to substantiate the validity of wind tunnel data. Wedding et al. (1980) developed a rigorous, analytically based model for predicting accurately the results of wind tunnel data for the Sierra dichotomous sampler inlet. The turbulence of the flow approaching the sampler is not considered by this model, which describes the behavior of particles after entering the inlet. In both the wind tunnel and the atmosphere, the sizes of the turbulent eddies are usually larger than the characteristic dimension of the inlet opening and are much greater than the particles' stopping distance. Even though atmospheric eddies are much larger than those in the wind tunnel, the inlet performances for the particle types tested could be expected to be similar in either regime. Wind tunnel test results, therefore, provide controlled testing environments for intercomparison of inlets, but to date have not yet been used to predict the mass concentrations realized in atmospheric situations.

Researchers such as McFarland and Ortiz (1979), Wedding et al. (1980), and Liu and Pui (1980) have designed and built such test facilities for characterizing aerosol samplers. From these tests, it is now recognized that ambient windspeed and direction can have a profound effect on particle sizes reaching the point of collection or measurement within the sampler. Without knowledge of these and related sampler characteristics, an accurate interpretation of the aerometric data is impossible. This section describes important characteristics for commonly used sampler types, so that the usefulness of aerometric data discussed in subsequent chapters can be assessed.

3.3.2 Gravimetric PM Mass Measurements

Techniques that employ direct gravimetric weighing of particles collected on a substrate are discussed separately here. Sampling techniques that fall into this category are extractive rather than *in situ*, in that the particles are removed from the airstream for subsequent analysis. Typically the ambient air is drawn into an inlet, transported to the collection substrate, often after one or more stages of particle size separation, and then deposited on a substrate by either filtration or impaction. In addition to the effect of internal separation stages, the particle size range collected by a filtration sampler depends on other parameters such as inlet geometry, internal wall losses, and the efficiency of the filter material. The high-volume sampler defined in the previous Air Quality Criteria for Particulate Matter (National Air Pollution Control Administration, 1969) and in the reference method for TSP (U.S. Environmental Protection Agency, 1979c) was considered to have captured all sizes of particles up to 100 μm (aerodynamic diameter). However, recent sampler characterization testing by Stevens and Dzubay (1975), Wedding et al. (1977), and McFarland and Rodes (1979) has shown that the gable roof used as an inlet and weather shield actually provides a D_{50} (the particle size at which 50 percent of the particle mass is passed on to the filter) of only 25 to 50 μm, depending on the windspeed. As shown by the data of McFarland and Rodes in Figure 3-4, the sampling effectiveness of the hi-vol sampler for large particles is substantially affected by ambient windspeed. Lundgren (1973) has examined the mass distribution of large particles up to 200 μm in the atmosphere as shown in Figure 3-3.

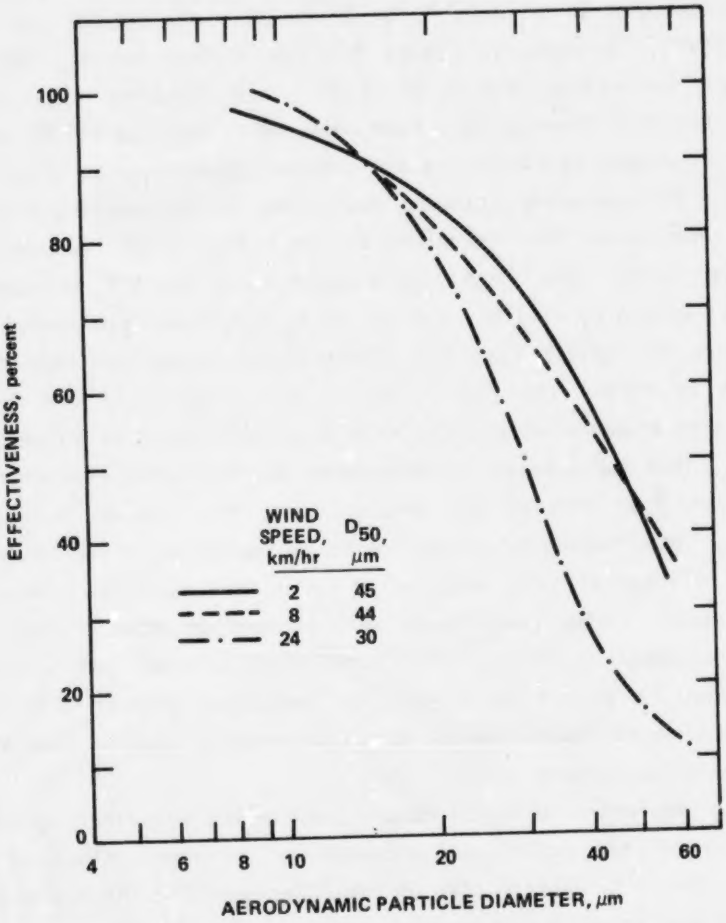

Figure 3-4. Sampling effectiveness of a Hi-Vol sampler as a function of wind speed. Sampler rotated at 1 RPM and operating at 1.4 m^3/min.

Source: McFarland and Rodes (1979).

Comparison of hi-vol sampler collection efficiency data in Figure 3-4 with these particle size distributions shows that the hi-vol sampler does not provide a true measure of the large particles in the atmosphere. Because particle mass increases as a cubic function of diameter for particles with constant density, the sampling of large particles must be treated carefully when considering a broad size distribution.

Size-specific sampler inlets designed to limit the particles collected to a certain size range are a relatively new technology for particles larger than 10 µm. Since these larger particles are difficult to transport in quantity, a sharp cutoff for large particles is not easily obtained except at high sampler flowrates using multiple stages of separation. The efficiency of a single stage inlet designed in 1977 (Stevens and Dzubay, 1978; see Appendix Figure 3A-1) to provide a 15 µm cutoff for a low flowrate sampler operating at 1.0 m^3/hr, (Wedding et al. 1977), is shown in Figure 3-5. Note that the D_{50} for this inlet is very windspeed dependent and varies from 9 to 22 µm. More advanced inlets (see Appendix Figure 3A-2 for diagram) for this flowrate have been designed by Wedding (1980) and Liu et al. (1980) and have reduced windspeed sensitivities and sharper cutpoints, as shown in Figures 3-6 and 3-7, respectively. The geometric standard deviations of the sampling effectiveness curves (a measure commonly reported in the literature of the sharpness of the size cut-off and denoted as σ_g) for these inlets vary from approximately 1.2 to 1.5 as compared to an ideal step-function inlet with a σ_g of 1.0. The use of σ_g should be interpreted as only an estimate of the slope, since it implies that the effectiveness versus particle size relationship is log-normal, which is rarely the case. Values of σ_g typically are determined either by dividing the particle diameter associated with an effectiveness of 84 percent into the D_{50} or by dividing the D_{50} into the diameter corresponding to 16-percent effectiveness.

After particles pass through the sampler inlet they can be lost from the flowstream before collection or measurement by attraction to or impaction on the internal surfaces of the sampler. Minimizing internal loss, especially for larger particles, requires careful design of the sample transport system geometry as well as consideration of factors such as surface charge dissipation. Wedding et al. (1977) reported internal wall losses in a prototype size-specific sampler to exceed 40 percent for particles greater than 15 µm. Loo et al. (1979) reported that recent improvements in the dichotomous sampler reduced internal particle losses to less than a few percent.

3.3.2.1 Filtration Samplers--The most commonly used method for direct gravimetric measurement involves collection of the particles suspended in a known volume of ambient air on a preweighed filter. The size distribution of particles reaching the filter are affected by the characteristics of the inlet, the transport system, and the separation stages, operating at the sampler flowrate. The performance of a sampler is also substantially affected by the filter characteristics. The efficiency of the filter medium used can influence the total mass collected if very small particles are not retained on the filter, or if very large particles bounce from the filter to subsequent stages. The collection efficiencies over a range of

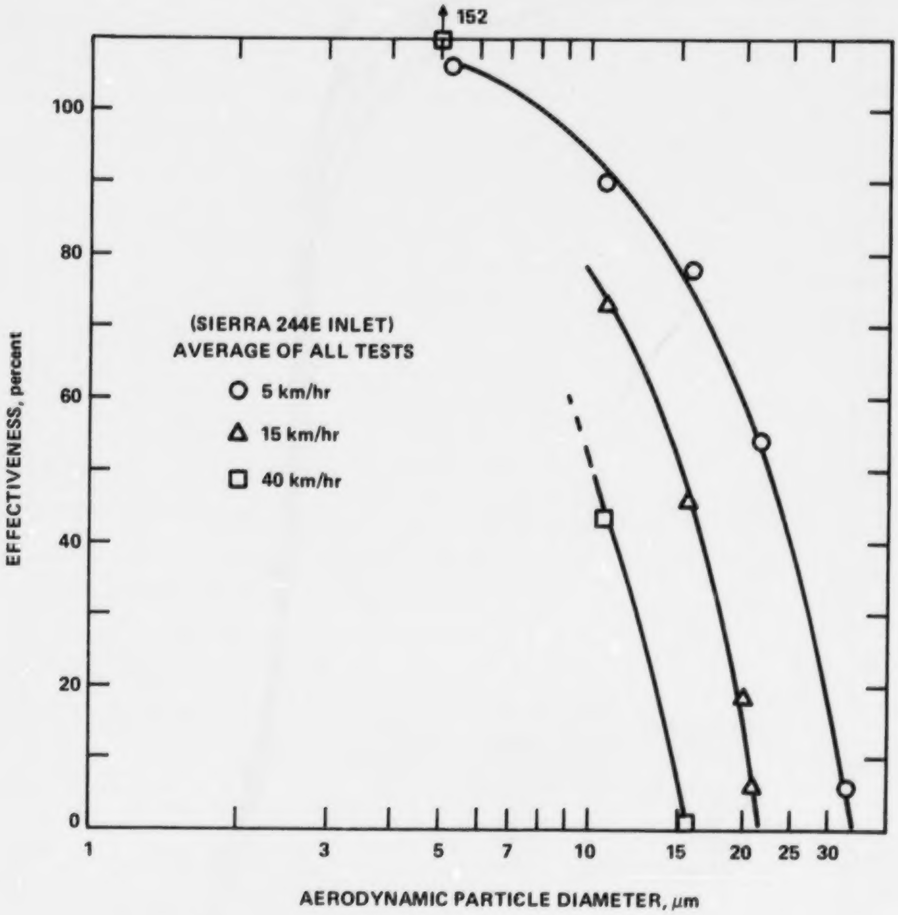

Figure 3-5. Sampling effectiveness of the dichotomous sampler inlet as a function of wind speed.

Source: Wedding et al. (1980).

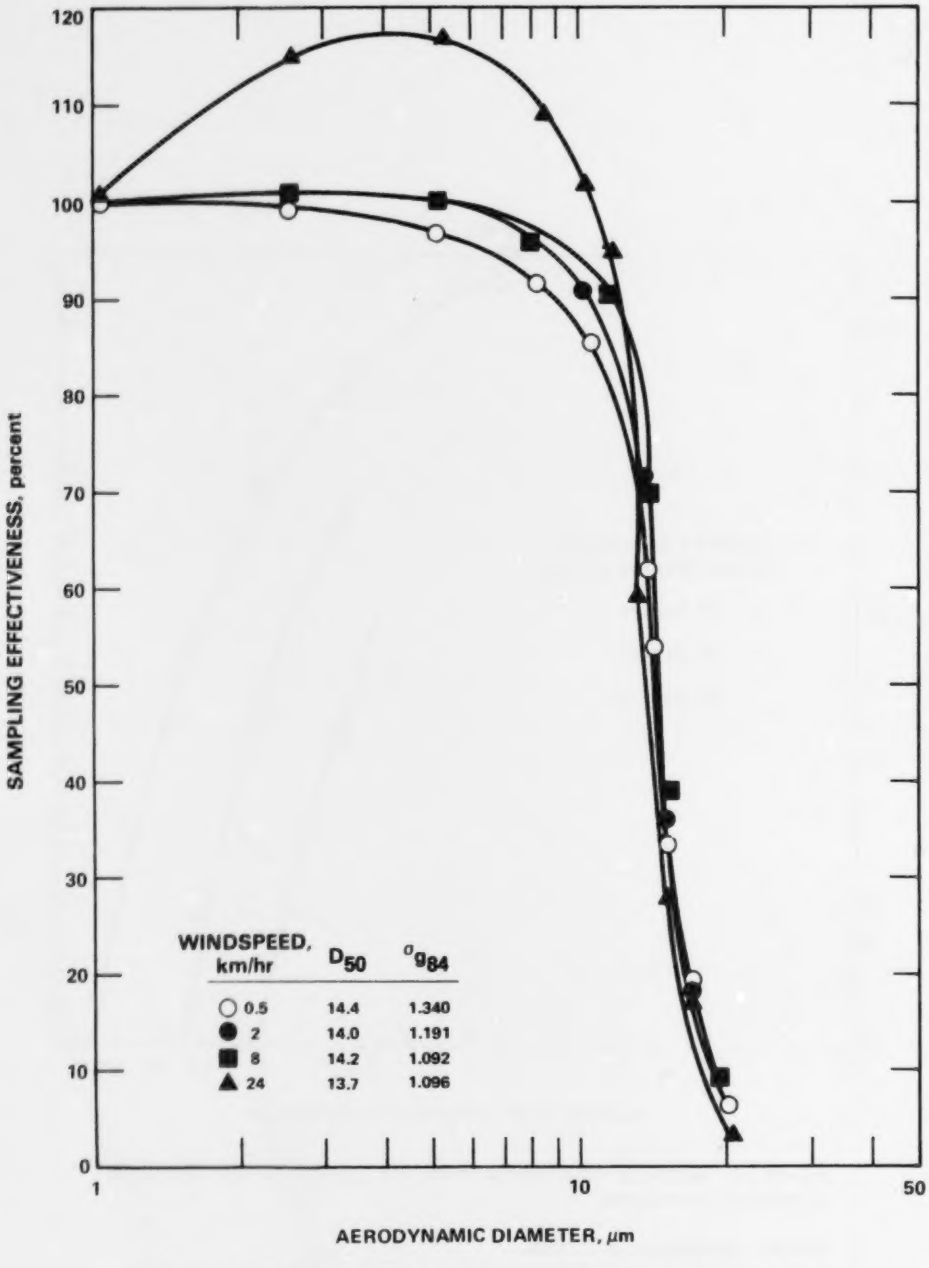

Figure 3-6. Sampling effectiveness of the Wedding IP inlet. Source: Wedding et al. (1980).

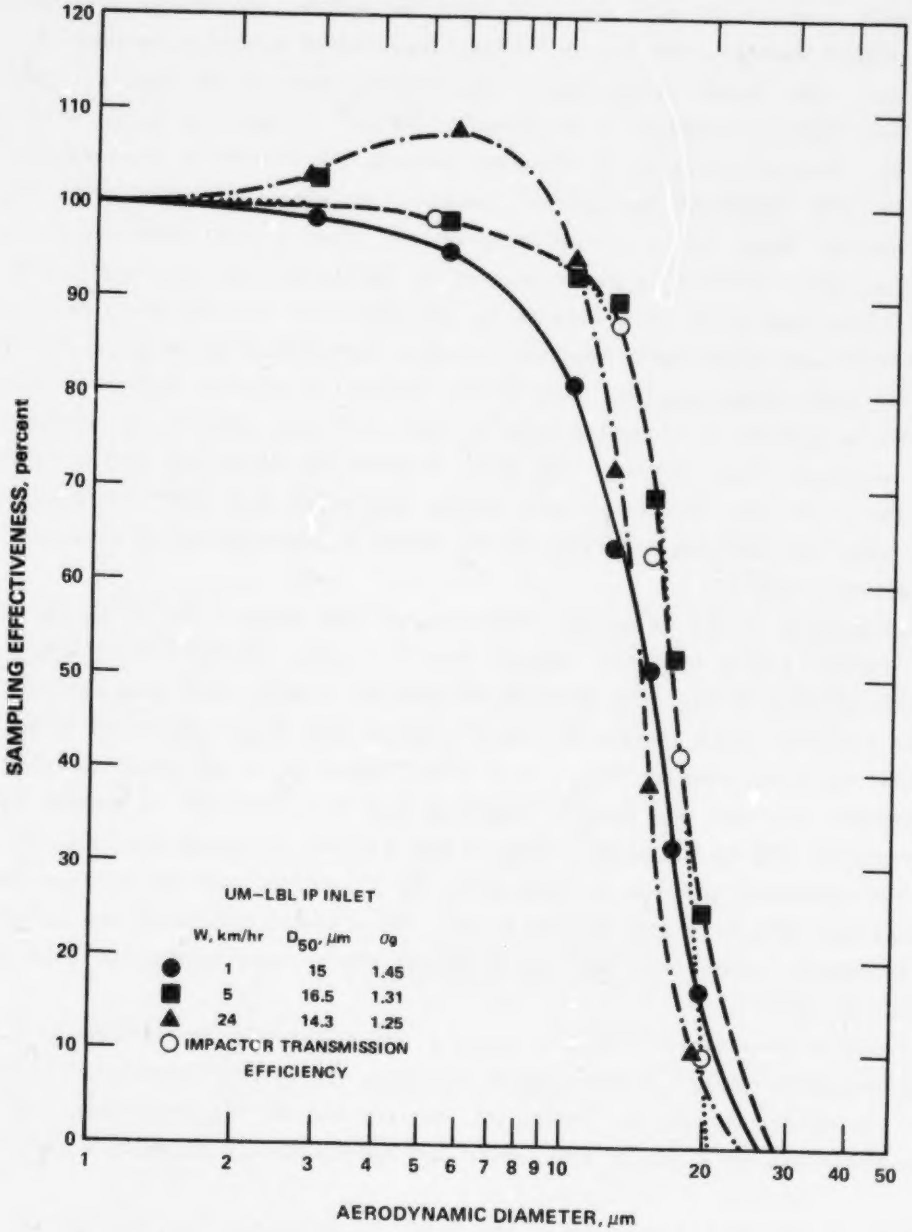

Figure 3-7. Sampling effectiveness of UM-LBL IP inlet.

Source: Liu et al. (1980).

particle sizes for a wide variety of filter materials, face velocities, and effective porosities have been determined by Liu et al. (1978a) for clean filters and by John and Reischl (1978) for exposed filters. Appendix Table 3A-1 tabulates selected fractional efficiency data for the commonly used TSP hi-vol sampler glass fiber filter, the Teflon® membrane filter used by the dichotomous sampler, and the cellulose fiber filter material (Whatman No. 1) used by the BS sampler. The latter filter shows some inefficiency at the smallest particle sizes, while the glass fiber and nominal 2 μm porosity Teflon® filters are highly efficient for all particle sizes. The relationship of flowrate through the filter to the pressure drop across it is also a very important mechanical consideration since this determines the available operating flowrate range for a vacuum pump of any given size. Membrane filter samplers, because of the rapid increase in pressure drop as particles deposit, require lower flowrates than fiber filter samplers. This results in substantially less PM being collected during a sampling interval and necessitates the use of a much more sensitive weighing device (balance).

3.3.2.1.1 TSP high-volume sampler. The hi-vol sampler is the EPA reference method for TSP. It is intended to operate at flowrates from 1.1 to 1.7 m^3/min, drawing air through a 200 x 250 mm (8 x 10 in) glass fiber filter. The mass of particles collected on the filter is determined from the difference between weights before and after exposure. The mass concentration is averaged over the sampling interval and is normally expressed in μg of mass collected per m^3 of air sampled (μg/m^3).

Although materials such as quartz fiber can be used, glass fiber is by far the most commonly used filter medium for this sampler and is nearly 100-percent efficient for 0.3 μm particles (Liu et al., 1978a). As noted by Friedlander (1977), this size particle is the most difficult to capture, since the collection of smaller and larger particles is accomplished by diffusion and impaction, respectively. This filter material is not prone to rapid overloading as is a membrane substrate and permits sampling over 24-hr periods in ambient TSP concentrations in excess of 300 to 400 μg/m^3. Glass fiber filters, although available in a variety of types, do not generally provide a chemically inert surface, and the surface impurities and basic pH may interfere with some measurements. The fibrous nature of the filter also makes surface measurements, such as X-ray fluorescence, impractical except for high atomic number elements such as lead.

The hi-vol is relatively simple to operate and reasonably inexpensive to purchase. The original method description in the Federal Register (U.S. Environmental Protection Agency, 1979c) was recognized to be an inadequate description of the procedure, and a much more detailed document was prepared by EPA (Smith and Nelson, 1973) to improve the quality of TSP data.

As shown in Appendix Figure 3A-3, the inlet is formed by the overhang of a gable roof which serves as a rainshield for the filter. The inlet effectiveness, as already discussed, does not produce a sharp particle size cutoff and is sensitive to windspeed. The collection efficiency of the hi-vol is also affected by sampler orientation (i.e., it is somewhat sensitive to wind direction) as described by Wedding et al. (1977). The average sampler flowrate is determined either by averaging single measurements before and after collection using an external flowmeter or by integration of a flow recorder trace. The effect of sampler flowrate on the sampling effectiveness for large particles as shown in Figure 3-8 is not substantial; however, use of a flow controller provides the most accurate sampler performance.

The absolute accuracy of ambient particle measurements such as those made by the hi-vol sampler cannot be determined directly with current technology. On the other hand, estimates of components of the overall accuracy can be determined, including the collection effectiveness of the sampler inlet and filter media and the accuracy of the flow measurement system. Two commonly used flow measurement devices on hi-vol samplers are the rotameter and the orifice meter with a pressure recorder. The rotameter is used to measure the initial and final flowrates from which an average is calculated. The pressure recorder provides a continuous trace of the orifice pressure drop that can be integrated for a more accurate measurement. Smith et al. (1978) using hi-vol samplers with both types of devices noted that the pressure recorder produced smaller errors (2 to 4 percent) when compared with a reference flow device than the rotameters (6 to 11 percent).

The precision of the hi-vol sampler as determined from collocated sampler measurements under field conditions and expressed by the coefficient of variation (cv) have been reported by several investigators. McKee et al. (1971) determined the cv for a measurement by a single analyst to be 3.0 percent while the same measure among multiple analysts in a collaborative test was 3.7 percent.

The design of the gable roof provides a settling chamber above the filter for larger particles blown in during periods when the sampler is not operational. McFarland and Rodes (1979) have determined this deposition experimentally as a function of particle size and ambient windspeed. Interpreting these relationships, however, requires knowledge of the existing ambient size distribution of particle mass. For a typical distribution, the amount of mass added to a hi-vol sampler filter during 5 days of exposure when it was not operational was predicted to be 6 to 8 percent. This effect has been measured in a field situation by Sides and Saiger (1976) and Lizarraga-Rocha (1976), who measured weight increases from 3 to 12 percent. Errors from this effect can be reduced by equipping the sampler with a mechanical device that keeps the filter covered during nonsampling periods. Timely installation and retrieval of filters will also minimize the problem.

As shown by Coutant (1977), Spicer and Schumacher (1979) and Appel et al. (1979), artifact PM can be formed by oxidation of acidic gases (e.g., SO_2, NO_2) or by retention of gaseous nitric acid on the surface of alkaline (e.g., glass fiber) filters and other filter types. The effect is a surface-limited reaction and, depending on the concentration of the acidic gas, should be especially significant early in the sampling period. The magnitude of the resulting error depends on such factors as the sampling period, filter composition and pH, and the RH. The magnitude and the significance of artifact mass errors are variable and dependent

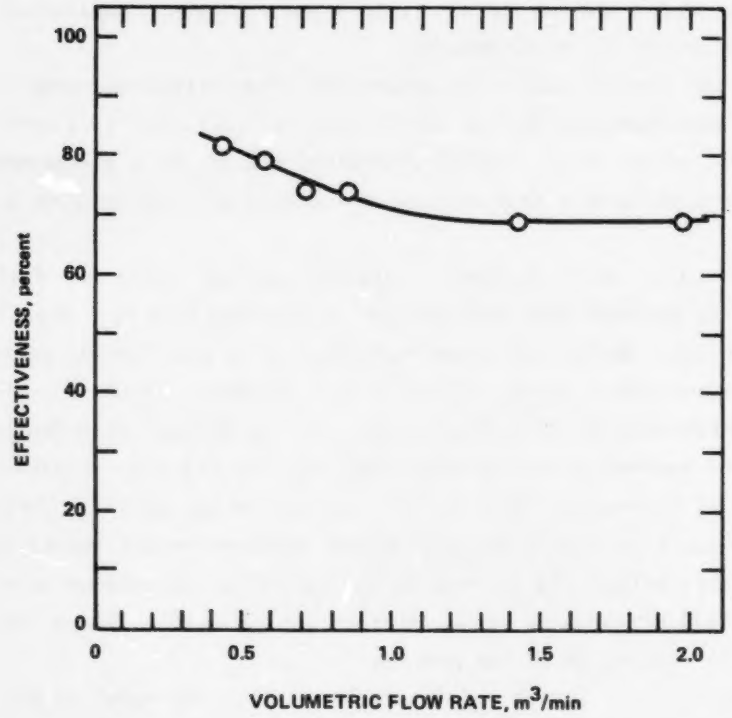

Figure 3-8. Effect of sampler flow rate on the performance of a Hi-Vol for 30 μm particles at a wind speed of 8 km/hr.

Source: McFarland and Rodes (1979).

on local conditions. Excluding the uncertainty associated with the collection and retention of organic particulate matter with appreciable vapor pressure, artifact mass primarily reflects the sum of the sulfates and nitrates formed by filter surface reactions with SO_3 and nitric acid gas, respectively. The ambient concentration of SO_2 is primarily dependent on fossil fuel combustion, while the nitric acid concentration is dependent on atmospheric photochemistry and, possibly, reactions in suspended water droplets (Orel and Seinfeld, 1977). A laboratory study by Coutant (1977) reported artifact SO_4 for 24-hour samples from 0.3 to 3 $\mu g/m^3$. Appel et al. (1978) observed up to 5 $\mu g/m^3$ artifact SO_4 on alkaline glass fiber filters in 24 hr laboratory exposures, and up to 3.2 $\mu g/m^3$ artifact sulfate in atmospheric trials at two California sites. Stevens et al. (1978) similarly found 2.5 $\mu g/m^3$ average artifact SO_4 based on sampling at 8 sites around St. Louis, Missouri; and Rodes and Evans (1977) noted 0.5 $\mu g/m^3$ artifact sulfate in West Los Angeles, California.

Artifact particulate nitrate values on glass fiber filters ranging from 1.9 to 26.4 $\mu g/m^3$ (mean 10.6 ± 6.9 $\mu g/m^3$, n = 13), were reported by Spicer and Schumacher (1979) in Upland, California. These values were obtained by comparison with nitrate concentrations measured simultaneously with quartz fiber filters. The likelihood of negative sampling artifacts on quartz fiber filters, as discussed below, make these artifact nitrate measurements upper limit values only. Appel et al. (1980) reported that artifact particulate nitrate on glass fiber filters is limited only by the gaseous nitric acid concentration. Such filters approximated total inorganic nitrate samplers, retaining both particulate nitrate and HNO_3 even when the latter was present at very high atmospheric concentrations (e.g., 20 ppb). Nitric acid was found to represent from approximately 25 to 50 percent of the total inorganic nitrate at Pittsburgh, Pennsylvania, and Lennox and Claremont, California. Based on an estimate of the most probable 24-hour artifact sulfate error (3 $\mu g/m^3$), and of the most probable artifact particulate nitrate (8.2 $\mu g/m^3$ in the Los Angeles, California, Basin and 3.8 $\mu g/m^3$ elsewhere) typical errors in mass due to SO_4 plus nitrate artifacts are estimated at 11.2 $\mu g/m^3$ in the Los Angeles Basin and 6.8 $\mu g/m^3$ elsewhere.

Nitrate salts can rapidly be lost from inert filters (e.g., Teflon, quartz) by volatilization (Appel et al., 1980; Forrest et al., 1980), and by reactions with acidic materials (Harker et al., 1977; Forrest et al. 1979). Loss of atmospheric nitrate from glass fiber filters occurs slowly. For example Smith et al. (1978) observed a 25-percent decrease in nitrate over 3 months in storage at room temperature accompanied by a corresponding loss of ammonium ion. Colovos et al. (1977) noted loss of up to 1.5 $\mu g/m^3$ NH_4^+ after 30 days storage. Immediate analysis after collection would minimize the significance of such loss.

In general, the hi-vol sampler data have been shown to be reproducible (3 to 5 percent), if an orifice meter and flow recorder are used. The sampling effectiveness for larger particles is windspeed dependent and, based on the data in Figures 3-3 and 3-4, the effect of windspeed could be estimated to produce as much as a 10-percent day-to-day variability for the same ambient concentration for typical conditions. The effect of the sums of the reported positive and negative artifact related to the glass fiber filter could be expected to add 6 to 7 μg/m^3 to the collected mass.

3.3.2.1.2 Dichotomous sampler. The dichotomous sampler collects two particle size fractions, typically 0 to 2.5 μm and 2.5 to about 15 μm, the latter cutoff depending on the inlet. This bimodal collection approximately separates the fine particles from the coarse particles as described in Chapter 2 to assist in the identification of particle sources. Since the fine and coarse fractions collected in many locations tend to be acidic and basic, respectively, this separation also minimizes potential particle interaction after collection.

The particle separation principle used by this sampler was described by Hounam and Sherwood (1965) and Conner (1966). As illustrated in a simplified fashion in Appendix Figure 3A-4, the separation principle involves acceleration of the particles through a nozzle, after which 90 percent of the flowstream is drawn off at right angles. The small particles follow the right angle flowstream, while the larger particles, because of their inertia, continue toward the collection nozzle. A separate 37 mm Teflon® filter is used for each fraction. The sharpness of separation is shown in Figure 3-9 from data by Loo et al. (1976) for a design cutpoint at 2.5 μm. Although cutpoints below 2.5 μm are mechanically impractical with dichotomous separators, 3.5 μm units are available commercially with equivalent cutpoint sharpness. A 2.5 μm cutpoint for the separator was recommended by Miller, et. al.(1979) because it provided good chemical separation between size fractions, satisfied the requirements of health researchers, and was mechanically practical. Inherent in the dichotomous separation technique is a contamination of the coarse particle fraction with a small percentage of the fine particles in the total flowstream. This is not considered a substantial problem for mass measurements and a simple mathematical correction as described by Dzubay et al. (1977) can be applied.

Teflon® membrane filters with porosities as large as 2.0 μm can be used in the sampler and have been shown to have essentially 100-percent collection efficiency for 0.3 μm particles (Liu et al., 1978a). Filters with smaller porosities, such as 0.5 and 1.0 μm, are also highly efficient, but are prone to much more rapid clogging as loading increases, accompanied by rapid decreases in sampler flowrate. Because the sampler operates at a flowrate of 1 m^3/hr (16.7 ℓ/min) and collects sub-milligram quantities of particles, a microbalance with a 1 μg resolution is required for filter weighing. Removal of the stickier fine particles causes the collected coarse particles to have a greater tendency to fall off the filter if care is not taken during filter handling and shipments (Shaw et al., 1979).

Dichotomous samplers are significantly more complicated to operate than single size fraction samplers and therefore are more prone to operator errors. As with the low flowrate cyclone samplers, the small mass collected on each filter requires careful weighing on a microbalance to provide reproducible results. The Beckman® inlet currently available for this sampler is shown in Appendix Figure 3A-1. Testing has shown that this inlet, as well as the essentially identical Sierra® inlet, are significantly windspeed sensitive, as shown in Figure

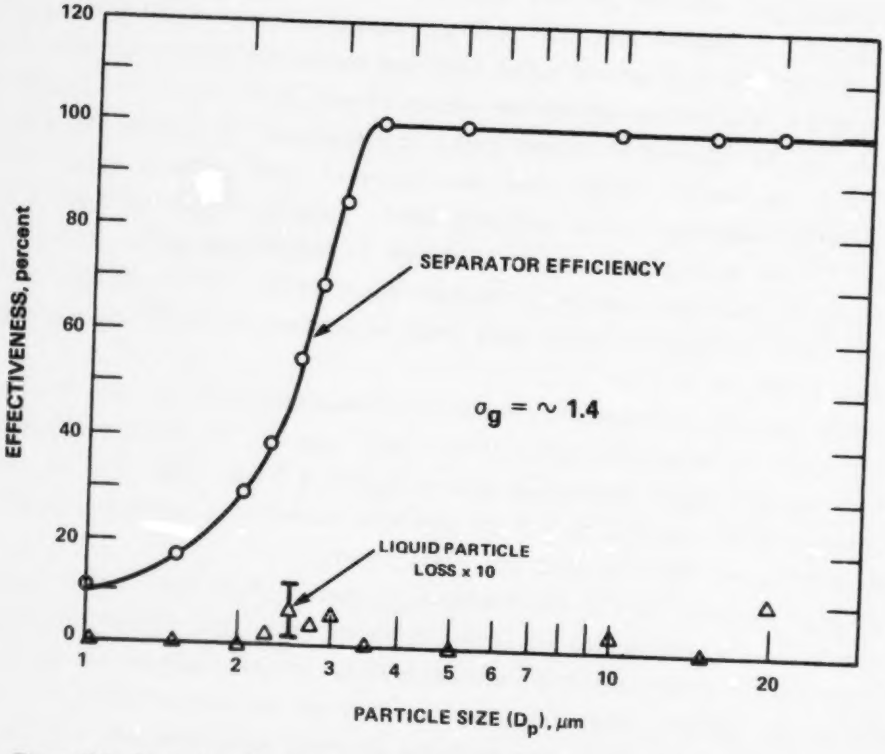

Figure 3-9. Separator efficiency and wall losses of the dichotomous sampler at 2 5 μm. Source: Loo et al. (1976).

3-5. As the windspeed changes, the D_{50} changes, resulting in variable collection of the larger particles. As noted earlier, inlets have recently been developed that have sharper cutpoints and are less windspeed dependent.

Automated versions of this sampler can automatically change the sampler filters to provide unattended operation. Depending on atmospheric concentrations, short-term samples of as little as 4 hours are possible with the automatic samplers to provide diurnal pattern information. The mass collected during such short sample periods, however, is extremely small and high variability of the results could be expected. With an inlet sampling effectiveness at 15 km/hr as described in Figure 3-5, the total mass collected would be 5 to 10 percent lower than the concentration collected by an ideal ($\sigma_g = 1.0$) inlet for a typical ambient size distribution such as the 60 $\mu g/m^3$ case shown in Figure 3-3. The overall reproducibility of dichotomous mass measurements is somewhat dependent on the care taken during filter handling and weighing, but could be expected to be about ± 10 percent.

3.3.2.1.3 Cyclone samplers. Ambient cyclone samplers are simple to operate and only moderately complex to build. Lippmann and Chan (1979) summarized the available cyclones for ambient particle sampling below 10 μm and noted that the separation effectiveness of cyclones can be designed to match respiratory deposition curves closely (see Figure 3-1). The cyclone separation principle can be applied to larger particle cutpoints, as demonstrated by Wedding et al. (1980) for a 15 μm sampler inlet. The small size of some cyclones makes them useful for personnel dosimetry sampling, if a suitably small pump and flow control system are employed. The Dorr-Oliver hydroclone, which is 10 cm in length and 10 mm inside diameter, matches the ACGIH curve (American Industrial Hygiene Association, 1970) and can be used for personal sampling. This cyclone has also been used in ambient field studies including the Harvard 6-City Study (Lioy, et al., 1980).

A cyclone sampler used in the Community Health Environmental Surveillance Studies (CHESS) (Barnard, 1976) is shown in Appendix Figure 3A-5. This sampler, as characterized in Figure 3-10, provides a relatively sharp separation with a D_{50} of 3.5 μm. The inlet of the sampler is the cyclone inlet, and a single 0 to 3.5 μm particle fraction is collected on the filter. The filter medium used in the CHESS network was glass fiber.

At an operational flowrate of 9.0 liter/minute, a typical fine fraction concentration of 30 $\mu g/m^3$ would result in the collection of only 390 μg of PM on the filter in 24 hours. At this level, Barnard (1976) determined the reproducibility of this sampler to be 13 percent. The effectiveness of the cyclone inlet for particles 3.5 μm and smaller should be nearly 100 percent. Use of the glass fiber filter would cause artifact mass problems similar to those identified with the hi-vol sampler.

Lippman (1970) discussed the effect of sample flowrate on the performance of cyclone samplers. Knight and Lichti (1970) compared the performance of the 10mm cyclone sampler to that of horizontal elutriators and noted that the results were comparable if the appropriate flowrates were used. Caplan et al. (1977) noted that five different flowrates, from 1.4 to

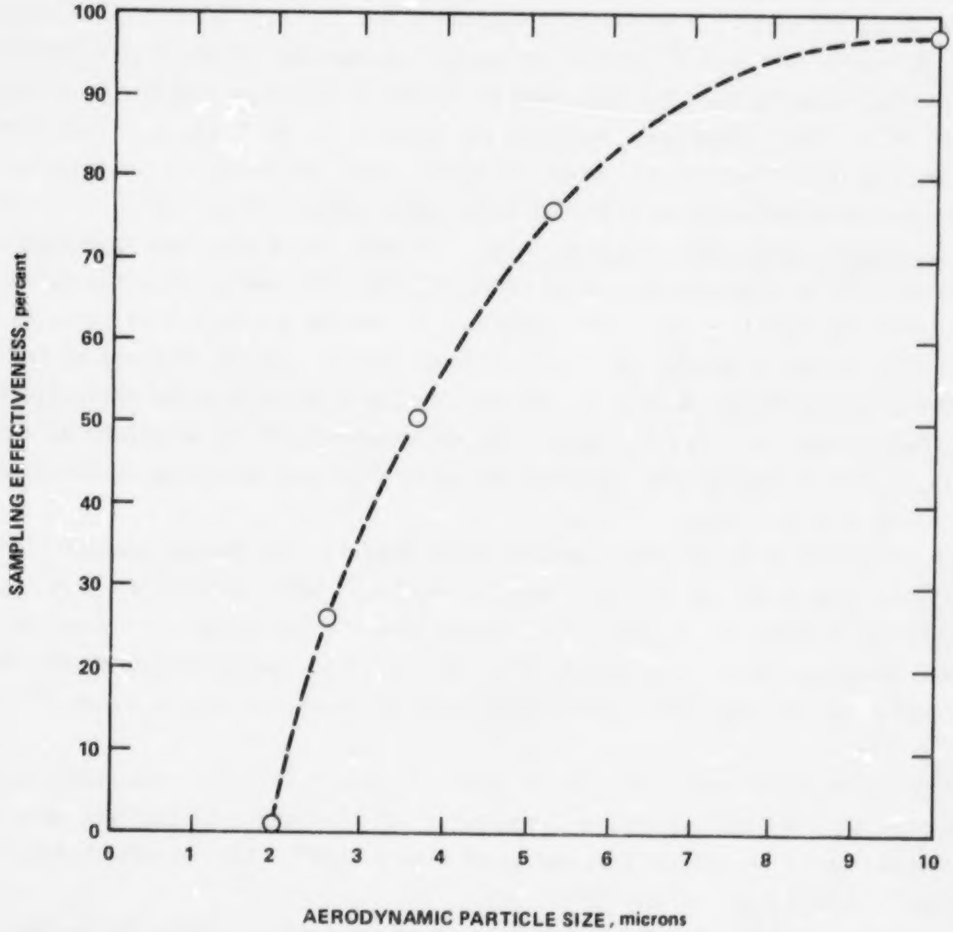

Figure 3-10. Sampling effectiveness for the 3.5-μm cutpoint CHESS cyclone sampler.

Source: Barnard (1976).

2.8 liter/minute, have been recommended by researchers since 1962 in order for this cyclone sampler to meet the ACGIH curve. They also noted that these small samplers are unaffected by ambient air velocity, dust loading, mass loading, orientation, or aerosol charge. The reproducibility of this sampler has not been given in the literature, but the low sampler flowrate and proportionately small aerosol mass collected may result in values greater than ± 10 percent.

Collection of the larger particles excluded by a cyclone sampler on a removable substrate is difficult, but alternative approaches, such as that designed by John et al. (1978) shown in Appendix Figure 3A-6, are available to provide a "total" sample dependent on the effectiveness of the inlet. The efficiency data for this cyclone as a function of sampler flowrate are shown in Figure 3-11 and indicate that sharp cutpoints are possible with current state-of-the-art units. A neutral pH Teflon® filter medium was recommended to minimize artifact mass formation. The inlet normally used for this sampler is the dichotomous sampler inlet shown in Appendix Figure 3A-1. This inlet was designed to operate at 16.7 ℓ/min. The windspeed influence on sampling effectiveness is shown in Figure 3-5. Reproducibility data for this sampler are not available but would be expected to be approximately 10 percent.

3.3.2.1.4 Hi-vol sampler with size selective inlet. To meet the monitoring requirements for Inhalable Particles (IP) as proposed by Miller et al. (1979), EPA commissioned the design of a size-selective inlet for existing TSP hi-vol samplers to provide a single 0 to 15 μm particle size fraction. This inlet is mounted on a conventional hi-vol sampler in place of the gable roof inlet. (See Appendix Figure 3A-7.) It has been tested by McFarland and Ortiz (1979) and has an inlet effectiveness as shown in Figure 3-12 and a sensitivity to windspeed as shown in Figure 3-13. Dry particle bounce and reentrainment were also reported to be insignificant at the sampler flowrate of 1.1 m^3/min.

The filter materials used are the same as those used for TSP hi-vol samplers, thereby presenting the same potential for artifact mass formation. This sampler, as with any size fractionating device, is somewhat sensitive to sampler flowrate for larger particles, as shown in Figure 3-14. However, these data suggest that special flow controlling measures are not necessarily required to maintain consistent collection efficiencies over a range of sampler flowrates.

The inlet effectiveness data shown in Figure 3-12 would indicate reasonably accurate particle collection with minimal windspeed dependence. The influence of artifact mass on the total mass collected could be expected to add about 6 to 7 μg/m^3. The reproducibility should be similar to the 3 to 5 percent of the TSP hi-vol.

3.3.2.1.5 Elutriator samplers. The British Medical Research Council (BMRC) (Orenstein, 1960) defined a respiratory system particle deposition curve (see Figure 3-1). This deposition curve is defined by the performance of a horizontal elutriator consisting of multiple parallel plates (Hamilton and Walton, 1961). A schematic diagram of this elutriator is shown in Appendix Figure 3A-8. This sampler has been used in Great Britain for ambient air sampling

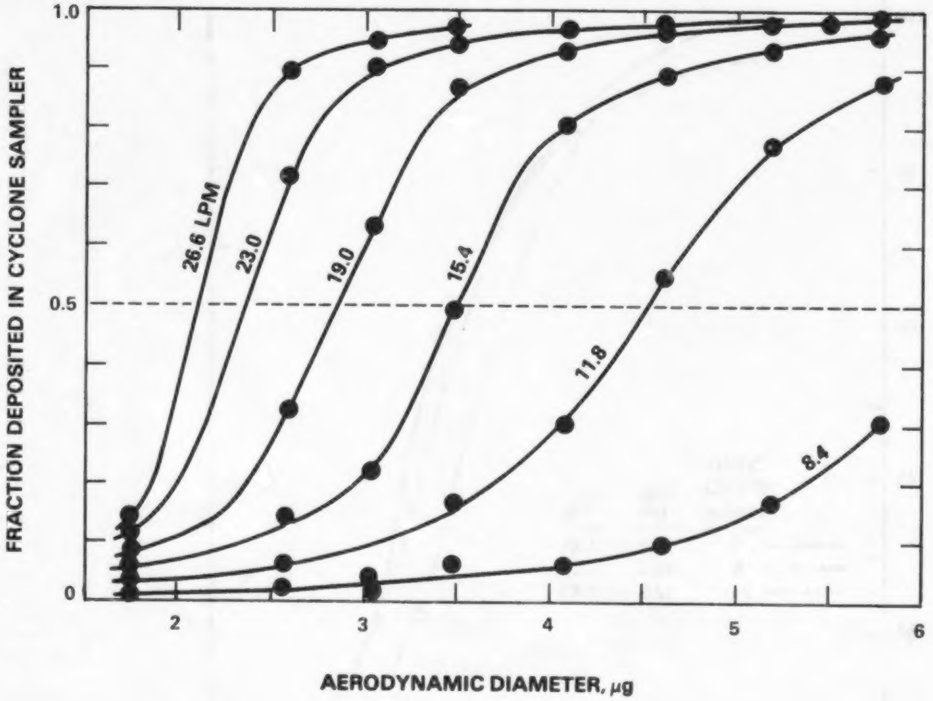

Figure 3-11. Fraction of methylene blue particles deposited in a cyclone sampler as a function of the aerodynamic particle diameter. Curves are labeled with flowrate in liters/min.

Source: John et al. (1978).

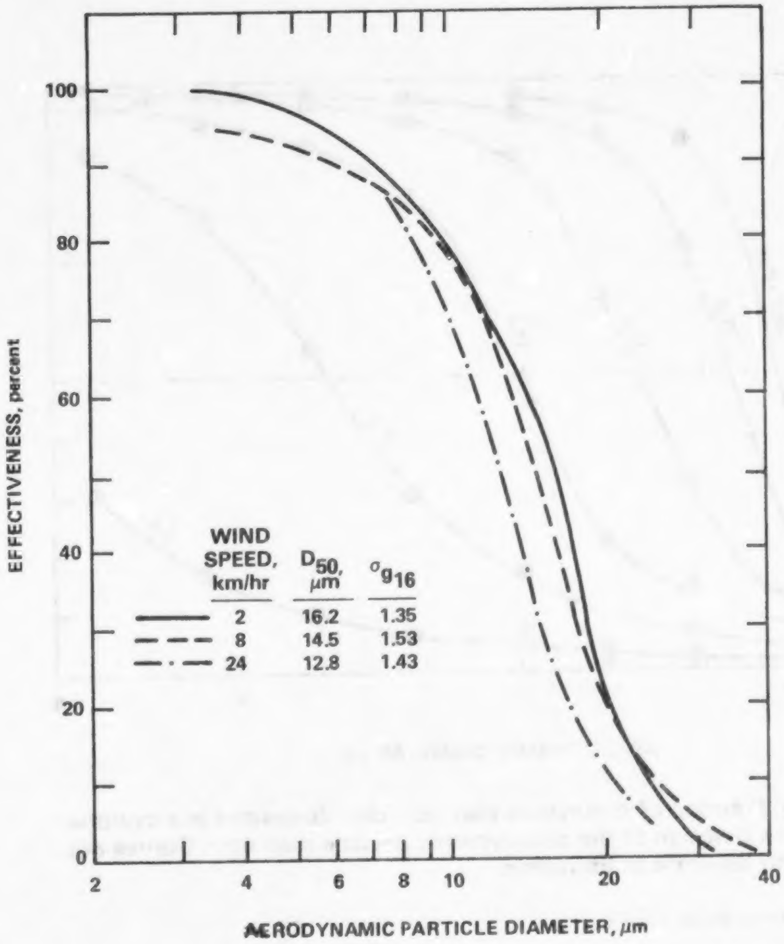

Figure 3-12. Sampling effectiveness for the size-selective inlet Hi-Vol sampler.

Source: McFarland and Ortiz (1970).

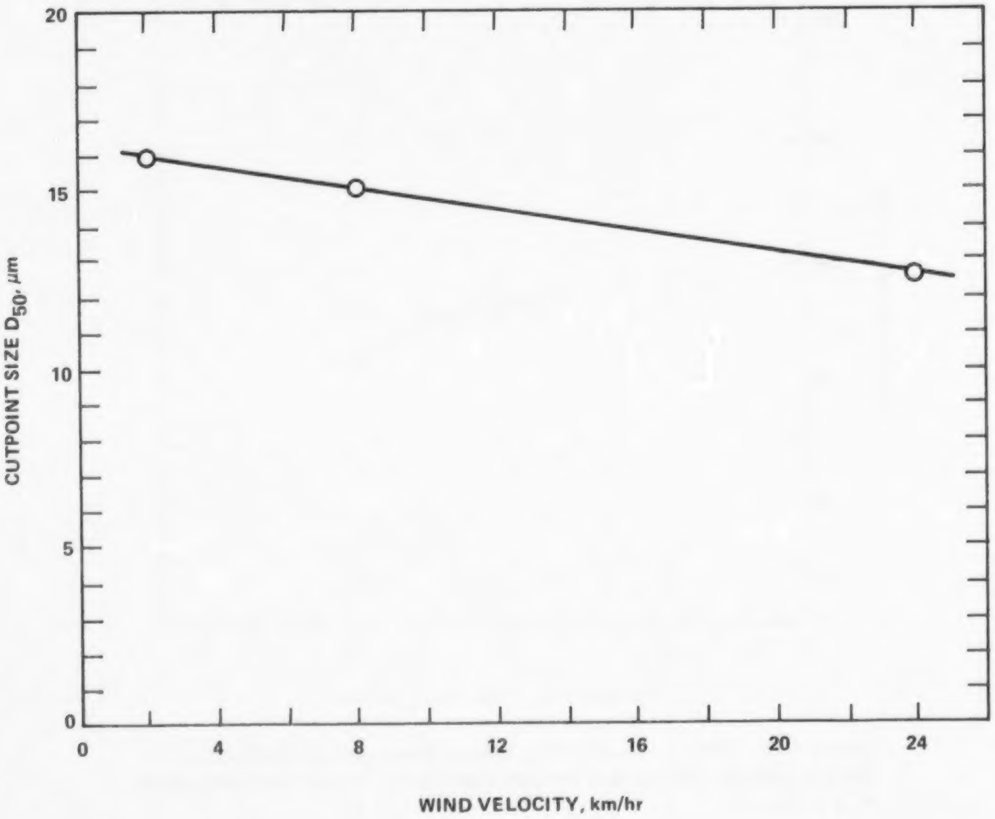

Figure 3-13. Effect of wind speed upon cutpoint size of the size selective inlet.

Source. McFarland and Ortiz (1979).

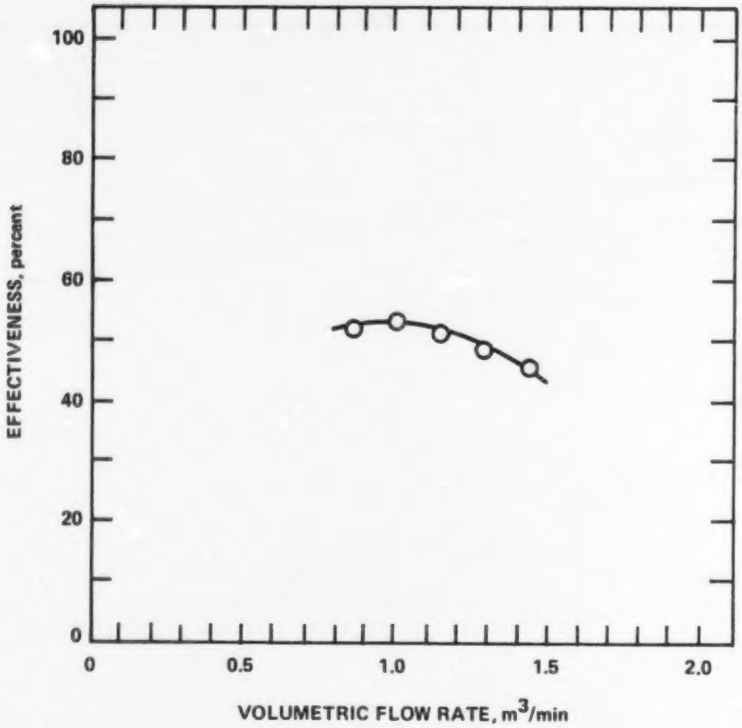

Figure 3-14. Effect of sampler flow rate on the sampling effectiveness of the size selective inlet Hi-Vol for a particle size of 15.2 μm and wind speed of 2 km/hr.

Source: McFarland and Ortiz (1979).

and during mining operations in the United States as an occupational exposure sampler. Corn et al. (1967) successfully used a horizontal elutriator to collect ambient particles below 3 μm selectively for optical examination on glass slides. Hamilton and Walton (1961) noted that reentrainment of coarse particles can be a problem in an elutriator if mechanical vibration exists. Because current ambient or wind tunnel test data on these samplers are not available, the reproducibility or accuracy cannot be estimated.

3.3.2.2 Impactor Samplers--Impactor samplers provide a means of dividing an ambient particle sample into subfractions of specific particle sizes. As shown in Appendix Figure A-9 for a cascade impactor the jet of air is directed toward a collection surface, which is often coated with an adhesive or grease to enhance collection. Large, high-inertia particles are unable to turn with the airstream and consequently impact against the collection surface. Smaller particles follow the airstream and can be directed either to another stage of impaction or collected on a filter. Use of multiple stages, each with a different particle velocity, provides collection of particles in several size ranges. Particle size distributions are constructed using impactor sampler data. (See Figure 3-3.)

Impactor samplers use removable impaction surfaces for collecting particles. Impaction substrates are weighed before and after exposure and typically are metal foil plates or glass fiber filters. The selection and preparation of these substrates have a significant effect on the impactor performance. Improperly coated or overloaded surfaces can cause particle bounce to lower stages, resulting in substantial cutpoint shifts (Dzubay et al., 1976). Marple and Willeke (1976) showed the effect of various impactor substrates on the sharpness of the stage cutpoint. Glass fiber substrates can also cause particle bounce and are subject to the formation of artifact particles similar to those on hi-vol sampler filters.

3.3.2.2.1 Cascade impactors. Cascade impactors typically have 2 to 10 stages, and commercial low-volume version flowrates range from about 0.01 to 0.10 m^3/minute. Lee and Goranson (1972) modified a commercially available 0.03 m^3/minute low-volume impactor sampler and operated it at 0.14 m^3/minute to obtain larger mass collections on each stage. Cascade impactors have also been designed to mount on a hi-vol sampler and operate at flowrates as high as 0.6 to 1.1 m^3/minute. A hi-vol sampler with a single impactor stage, shown in Appendix Figure 3A-10, was used in the Community Health Air Monitoring Program (CHAMP) and operated at 1.1 m^3/minute.

Particle size cutpoints for each stage are dependent primarily on sampler geometry and flowrate. The smallest particle size cutpoint routinely used is approximately 0.3 μm, although special low-pressure impactor samplers such as that described by Hering et al. (1978) are available with cutpoints as small as 0.05 μm. A high-efficiency filter typically is used after the last impaction stage to collect the small particles not impacted previously. The masses collected on each stage plus the backup filter mass collection are often reported, as shown in Figure 3-15 from data by Lee (1972). This cumulative distribution format permits determination of the Mass Median Diameter (MMD), at which point 50 percent of the mass is smaller than the indicated size. Use of straight line plotting techniques (as shown in Figure

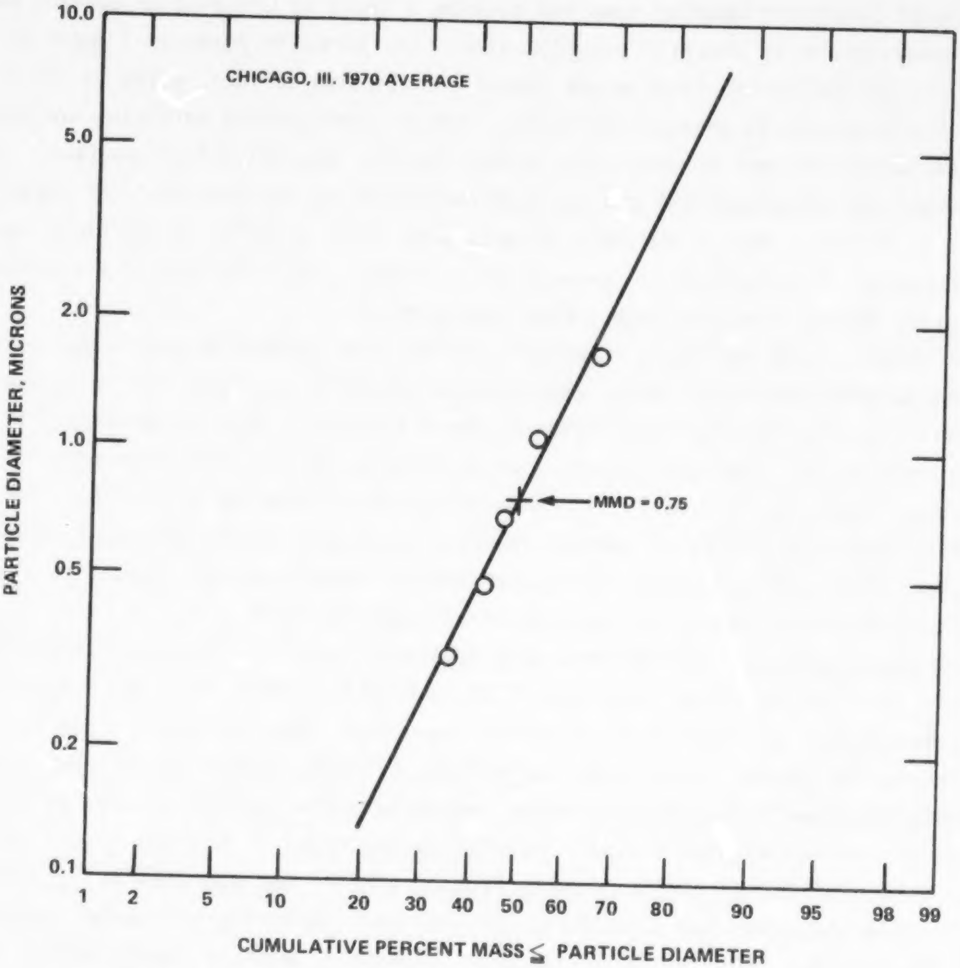

Figure 3-15. An example of a mass size distribution obtained using a cascade impactor.

Source: Lee (1972).

3-15) implies a log normal mass distribution, which can result in misinterpretation of the mass median diameter.

Cascade impactors are not normally operated in routine monitoring networks because of the manual labor required for sampling and analysis. Although impactor sampling systems are not extremely complex, careful operation is required to obtain reliable data, especially if coated collection surfaces are used. Analysis of constituents other than mass to obtain size distributions of species such as sulfates are possible, but require careful analytical techniques or compositing by stage with other samples to obtain an adequate quantity of material for analysis. Impactor stages that use grease coatings may prove undesirable for certain analyses because the grease may interfere with the method. Natusch and Wallace (1976) investigated the errors associated with impactor sampling and concluded that even under very unfavorable conditions the MMD can be determined to well within 25 percent of the true value.

The inlet characteristics of most impactors have not been determined, resulting in uncertainty about the size range of particles sampled. McFarland (1980) examined the inlet of the NASN low-volume (0.14 m^3/min) cascade impactor and determined that particles larger than 10 µm were unlikely to reach the collection stages because of substantial wall losses. Willeke and McFeters (1975) characterized the CHAMP hi-vol sampler inlet under static windspeed conditions, as shown in Figure 3-16. If the characteristics of the impactor inlet are known, the total mass collected by the sampler can be used for comparison with other similar size-specific measurements.

The particle separation of an impactor stage can be very sharp, and mathematical models are available to permit stage sizing at selected cutpoints. The single impaction stage of the CHAMP hi-vol sampler designed to be 3.5 µm was characterized by Ranade and Van Osdell (1978) and demonstarted a reasonable agreement with theory (Figure 3-17). Note, however, that solid particles above 5 µm deviate from the relationship, indicating possible particle bounce effects.

3.3.2.2.2 Rotary inertial impactors. Whereas cascade impactors draw the fluid stream to the impactor surfaces, rotary inertial impactors move the impactor surfaces through the fluid. The impactor surfaces, which are spun by an electric motor, are coated with a sticky film and collect particles with diameters greater than about 1 µm by inertial impaction. The collection efficiencies of such samplers, which include the Rotorod (Balzer, 1972) and the Noll rotary impactor (Noll, 1970), are based on the Stokes number (Fuchs, 1964).

Using rectangular glass slide collectors, at a rotational speed of at least 35 m/sec (78 mph), Noll (1970) measured efficiencies of 85 to 100 percent for particles from 6 to 108 µm. The collection efficiencies are windspeed independent if the rotational velocity of the impactor surfaces is large compared to the ambient windspeed.

Microscopic counting techniques are used to determine the particle distribution on the collector. The sample volume is the volume swept by the stage during the sampling interval. Variations of this design principle include exposed wires and plates extended from moving vehicles such as boats and airplanes.

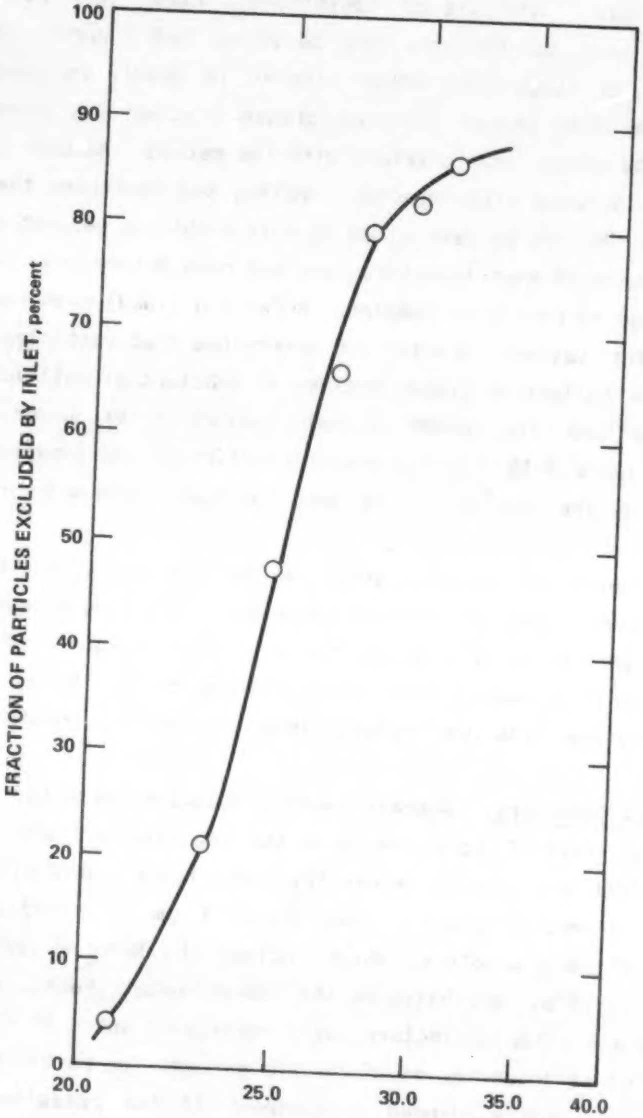

Figure 3-16. Fractional particle collection of the CHAMP fractionator inlet at a sampler flow rate of 1133 liters/min. under static windspeed conditions.
Source: Willeke and McFeters (1975).

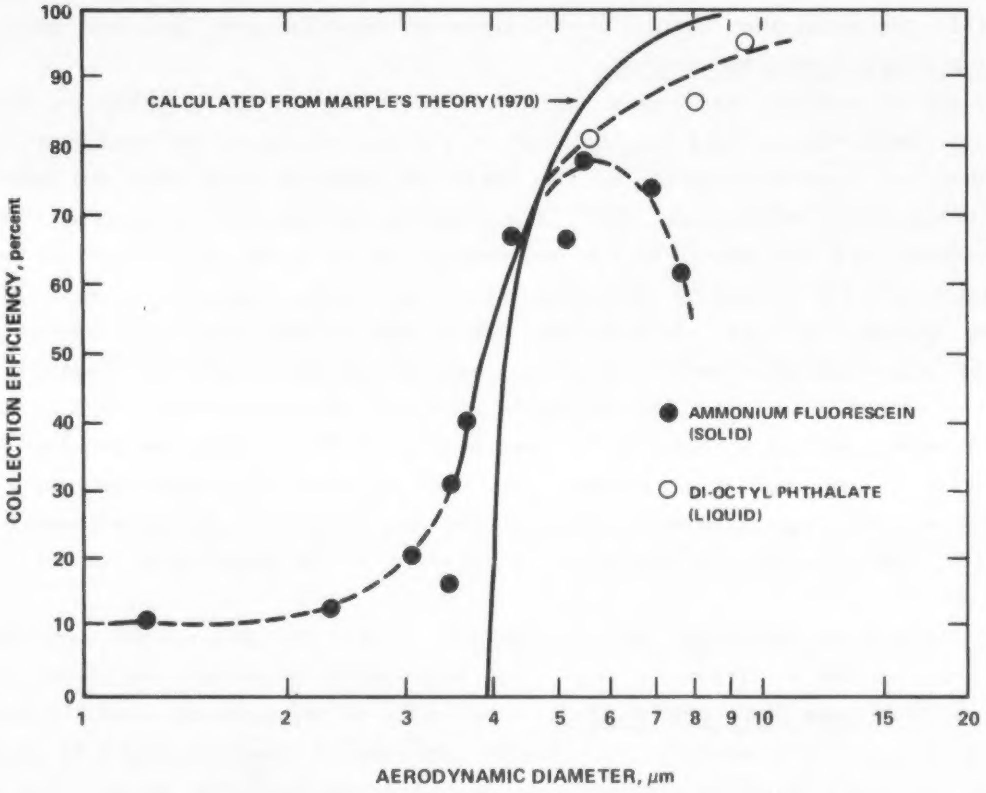

Figure 3-17. Efficiency of the single impaction stage of the CHAMP Hi-Vol sampler.

Source: Ranade and Van Osdell (1978).

The advantage of this type of sampler is that it eliminates inlet biases associated with aspirated samples, especially for particles > 10 μm in turbulent air. Because of the amount of labor required to measure large-particle size distributions, they are not practical for routine use in networks.

3.3.2.3 Dustfall Sampling--Since very large suspended particles have appreciable settling velocities, they are collected by deposition in a dustfall container and weighed as described by the American Society for Testing and Materials (1981a). Although a cylindrical jar might be expected to collect the equivalent of the dust content of an air column of its own diameter extending to the top of the atmosphere, the aerodynamic effects of the jar, the angle of approaching windflow, the mounting brackets for the jar, and adjacent structures tend to complicate the collection pattern. As noted by Nader (1958), it is difficult to interpret the meaning of dustfall data and the significance of correlations with other measurements. The most recent evaluation of available dustfall measurement techniques was reported by Köhler and Fleck (1966), who noted that typical coefficients of variation were less than ±10 percent.

3.3.3 Non-gravimetric Mass Measurements

A variety of particle measurement techniques other than direct weighing are available. Many of these techniques collect the particles on a filter substrate, followed by an analysis that measures an integral property of the deposited particle other than the total mass. Examples include light reflectance, light transmittance, and beta-ray attenuation. Other *in situ* measurements are also used, which do not deposit the particles on a filter but measure a characteristic of the suspended particles, such as light scattering. Most of these alternative methods are less expensive per sample and provide more rapid collection and analysis of data than gravimetric analysis. Some measurements are not generally useful because they depend heavily on site-dependent particle characteristics, such as color or density. In most cases, a scientifically-based physical model relating the integral measurements to mass is not available, thereby providing no basis for regression analysis. A site-by-site best-fit regression must then be considered, which provides questionable accuracy in predicting the true mass concentration, especially if the composition of the local PM changes with time.

3.3.3.1 Filtration and Impaction Samplers--Samplers in this category collect particles on a substrate and then use an alternative analytical technique as a surrogate to direct weighing.

3.3.3.1.1 British Smoke Shade sampler (BSS). The design of the currently used BSS sampler is based in part upon early work by Hill (1936), who used transmitted light to assess the darkness of the stain resulting from particle collection on the filter paper. This sampler draws an airstream upward through an inverted funnel and 3 meters of nominal one-quarter-inch diameter plastic tubing to an inverted filter holder containing a Whatman No. 1 cellulose fiber filter. As noted earlier, the Whatman filter medium has been shown to be somewhat inefficient when sampling very small particles (Liu et al., 1978a). A schematic diagram of a version of this sampler designed to collect sequential samples for 8 days is shown in Appendix Figure 3A-11. A bubbler is often used downstream of the filter holder for subsequent SO_2 measurements. The sampler is operated at approximately 1.5 liters/minute, which is verified by a dry test meter built into the sampler. The filter holder can be 25, 50, or 100 mm in diameter to collect a spot of the proper darkness range for subsequent measurement by reflectance.

Since the early 1900's, many studies have been conducted in order to establish relationships between smoke shade reflectance readings and gravimetric measurements. A 1964 study supported by the OECD established the currently used relationships between smoke shade reflectance measurements and gravimetrically determined particulate concentrations. These data were accepted by the WHO (1976) and compiled into a standard operating procedure for reporting smoke shade measurements in equivalent $\mu g/m^3$. These equivalent mass concentrations are not determined by weighing the smoke shade sampler filter but through comparison with a collocated gravimetric sampler. The gravimetric measurements that were made for OECD and compared to the smoke shade measurements were called "high-volume sampler" readings, but were not taken with the U.S. TSP hi-vol sampler. The OECD gravimetric "high-volume sampler" as described by the British Standards Institution (1964) operates at approximately 60 liters/minute, compared to the 1.5 m^3/minute of the U.S. hi-vol sampler. The OECD hi-vol was designed to be aerodynamically similar to the smoke shade unit but has not been characterized for aerosol collection effectiveness. Prior to 1964, various calibration curves were published relating smoke shade reflectance to mass estimates in nominal $\mu g/m^3$ units, but it is difficult to compare these earlier relationships to the OECD version.

McFarland (1979) examined the aerosol collection properties of the smoke shade sampler and produced the effectiveness plot shown in Figure 3-18, which shows that the D_{50} for particles reaching the filter (entire system) is only about 4.5 μm. A comparison of the "entire system" data with the deposition models given in Figure 3-1 shows a coincidental agreement within 1 μm of the ACGIH and Los Alamos curves. Most large particles are either rejected at the inlet or lost in the inlet line, although some particles as large as 10 μm do reach the filter. Because the size range of particles collected by the smoke shade sampler is substantially less than that collected by the TSP hi-vol sampler, results of comparisons between the methods could be expected to vary.

Ball and Hume (1977) and Waller (1963) noted that consistent relationships can be developed, but are site, season, and particle-source dependent. Lee et al. (1972) noted, from collocated TSP hi-vol and smoke shade sampler comparisons made at various sites in England, that the overall correlation coefficients between these measurements for all sites was 0.618. However, the individual coefficients ranged from 0.936 (good correlation) to 0.072 (no correlation). Bailey and Clayton (1980) showed that smoke shade measurements correlated more closely with soot carbon content than with gravimetric mass. Recent work by Edwards (1980)

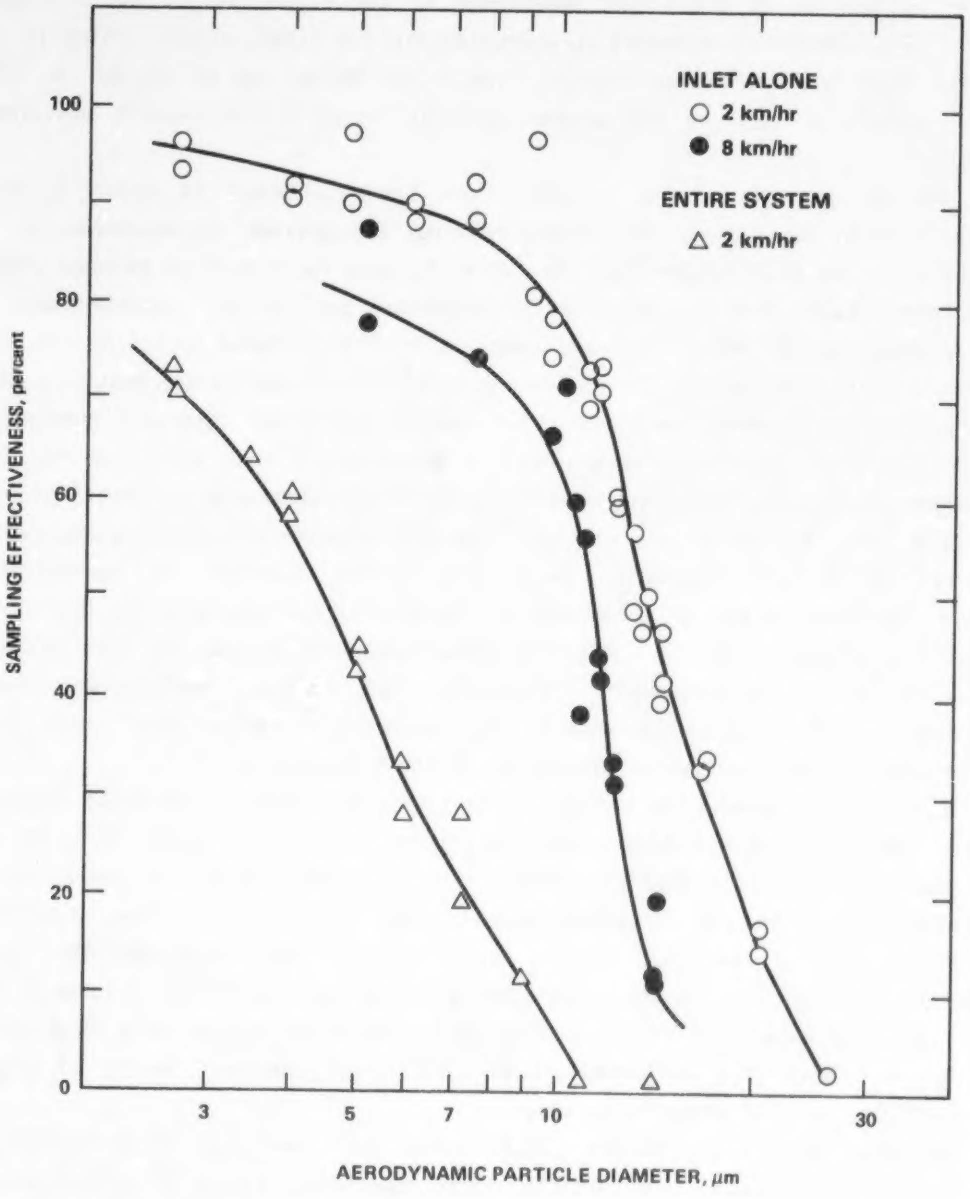

Figure 3-18. Sampling effectiveness of the inlet alone and through the entire flow system of the British Smoke Shade sampler.

Source: McFarland (1979).

has shown that smoke shade reflectance measurements can be related to the absorption coefficient of the atmosphere. This work also showed that smoke shade measurements can be converted to approximate COH measurements made by the American Iron and Steel Institute (AISI) tape sampler (see Section 3.3.3.1.2) using the absorption coefficient relationships. As several investigators noted, (e.g., Lodge, et al. 1981), if a relationship could be developed between optical and gravimetric measurements, it would be site specific but still variable because of seasonal and long-term differences in the sources of collected particle size fractions and their carbon content. The smoke shade sampler is relatively simple and inexpensive to use for routine monitoring. The British Standards Institution (1964) reported the reproducibility of collocated smoke shade sampler measurements as 6 percent. The accuracy of a given relationship's predicted mass concentrations from reflectance measurements cannot be discussed in general terms because of the previously mentioned confounding influences. Subsequent use of smoke shade results elsewhere in this document (Chapter 14) will discuss the accuracy of the measurements relative to the specific studies evaluated there.

3.3.3.1.2 Tape sampler. A variation of the optical measurement of spot darkness is the use of a continuous filter tape and an automatic tape advancing system. A sampler using this approach, developed by Hemeon (1953) for the AISI, samples at a flowrate of approximately 7 liters/minute using Whatman No. 4 filter paper and collects particles on a 25 mm filter spot. The spot darkness is read either by a transmittance or reflectance measurement. Transmittance measurement is most popular in the United States.

The AISI tape sampler typically collects particles in selected time intervals of 1 to 4 hours, and then advances to an unexposed clean portion of the tape. Optical measurements are referenced to an unexposed filter area and can be made either external to the sampler after sample collection or with a continuous readout self-contained in the sampler.

Transmittance measurements are converted to optical density through a Beer's Law relationship and then to CoH units per 1000 linear feet of air sampled. A CoH is defined as the quantity of PM on the paper tape that produces a change in optical density of 0.01. The alternate Reflectance Unit of Dirt Shade (RUDS) is equivalent to 0.1 CoH units per 1000 feet (American Society for Testing and Materials, 1981b).

As shown in Appendix Figure 3A-12, this sampler uses a funnel inlet and a small diameter transport tube nearly identical to the British Smoke Shade sampler. Although the two samplers operate at different flowrates, the particles reaching the filter tape could be expected to have a size range similar to that illustrated in Figure 3-18.

The utility of the sampler to estimate mass concentrations has been investigated by many researchers, usually in comparison with the TSP hi-vol sampler. Since these two samplers do not collect similar particle size ranges, such comparisons could be expected to vary unless only a small proportion of coarse particles are present. Regan et al. (1979) as well as others have shown with field data that the correlation improves substantially when the tape sampler data are compared with smaller particle fractions such as the 0-2.5 μm fine fraction. As noted in the discussion of the smoke shade sampler, the accuracy of a relationship between AISI readings and mass concentration for a given data set is difficult to predict.

3.3.3.1.3 Beta-ray attenuation. Beta-ray attenuation is another technique for estimating the mass of particles collected on a filter, without direct weighing. An exposed filter is placed between a low-energy beta-ray source, such as ^{63}Ni, ^{14}C, or ^{147}Pm, and a beta detector is used to measure the amount of attenuation caused by the particle as compared to a clean filter. A set of gravimetrically prepared standards are used to relate the results to units of mass. This method is useful because it can be automated to handle a large number of samples (Goulding et al., 1978; Loo et al., 1978). Real time mass measurements are also feasible (Macias and Husar, 1976).

Investigators (Macias and Husar, 1976; Goulding et al., 1978) have studied the dependence of the beta-ray absorption coefficient on elemental composition of the sample. Goulding et al. (1978) found the dependence on composition to be reasonably small for the ranges of average compositions that occur in aerosol samples. In a recent interlaboratory comparison of aerosol sampling and measurement methods (Camp et al., 1978), it was demonstrated that laboratory beta gauge measurements of ambient aerosols collected at one site by dichotomous samplers on Teflon® filters compared favorably in precision and accuracy with concurrent gravimetric analyses. Principal sources of error in the method are possible changes in the orientation of the filter substrate between the pre- and post-sampling measurements and changes in attenuation because of absorption of water from the atmosphere by the filter material or the collected particulate matter (Lawrence Berkeley Laboratory, 1975).

Jaklevic et al. (1981), after an extensive evaluation of the technique, have concluded that the precision is typically better than 5 μg/cm^2 for a variety of sample types, assuming reasonable care in laboratory manipulation. The precision and accuracy are significantly better for samples of fine particles only, since one of the major causes of deviation from ideal behavior is the presence of a significant number of larger particles. The possibility of automating the process makes it particularly attractive for laboratories handling large numbers of samples. Especially considering the latter advantage, it is not seriously inferior to gravimetric techniques. In some cases it may be superior in precision and accuracy to weighing very lightly loaded samples by hand on a microbalance, since it is insensitive to such errors as those caused by loss of small fragments from the edges of the filters.

3.3.3.1.4 Piezoelectric microbalance. The piezoelectric microbalance technique collects particles on an oscillating quartz crystal, either by impaction or electrostatic precipitation. The frequency change of the crystal oscillation is proportional to the mass collected and the rate of change in frequency is proportional to the mass concentration (Woods, 1979). Advantages of the piezoelectric detection principle, as noted by Lundgren et al. (1976), include extreme sensitivity and real time response. The technique can also be applied in a multiple stage impactor form, using crystals as the collection plates. This approach provides rapid determination of particle size distributions.

Disadvantages of this detection principle include the need for frequent cleaning of the crystal and severe interference from large RH changes and nonlinearity of crystal response to large particle concentrations. As shown by the data of Lungren et al. (1976) in Figure 3-19, the effect of humidity depends on particle type and is, therefore, nearly impossible to predict. Daley and Lundgren (1974) studied the potential errors in piezoelectric detection and noted that although not currently used as a routine monitoring method, it can be used sucessfully for short-term studies when realistic operating limits are observed.

3.3.3.2 In Situ Analyzers--Instead of collecting particles on a filter before analysis, certain aerosol characteristics can be examined while the particles are still suspended in the airstream.

3.3.3.2.1 Integrating nephelometer. The integrating nephelometer measures the optical scatter caused by suspended particles in the airstream. The initial designs for this technique were made by Beuttell and Brewer (1949) and subsequently improved by Ahlquist and Charlson (1967). The nephelometer is calibrated using the known scattering coefficients of gases such as Freon 12 (CCl_2F_2). Light scattering is at a maximum for particles in the 0.3 to 0.8 µm size range as shown in Figure 3-20. Accumulation mode particles are the primary cause of light scattering, which is only slightly affected by particles in the nucleation or coarse particle modes (Waggoner, 1973). Visual range can also be calculated from the scattering coefficient using a relationship developed by Koschmieder (1924).

Correlation of optical scattering with hi-vol suspended particle mass would be possible only at sites where coarse particle mass concentrations are low or correlated with accumulation mode particle mass. From theoretical models (Waggoner et al., 1973), there should be a high site-independent correlation between fine particle mass loading and optical scattering. Waggoner and Weiss (1980) and Groblicki et al. (1980) have reported correlations above 0.95 between gravimetric fine particle mass and nephelometric measurement of scattering extinction. Their measurements found the same ratio of scatter to fine mass at an urban and a rural Colorado site, as well as at a Pacific coast site in Washington. Nephelometric scattering extinction appears to be a useful indicator for fine particle mass but will provide erratic results when compared to any particle measure that contains coarse particle mass. A comprehensive discussion of the nephelometer as a visibility monitor is contained in Chapter 9.

3.3.3.2.2 Condensation nuclei counter. The condensation nuclei counter measures the total light scatter of submicron particles whose size has been increased by condensing vapor onto their surface in a cloud chamber. This device is of interest in determining the number concentration of particles in the nuclei mode but is not normally used for particle sizes above about 0.5 µm (Perera and Ahmed, 1978). It is often used in conjunction with prior size separation stages to obtain a particle size distribution for submicron size particles. The condensation nuclei counter is rarely used for routine monitoring.

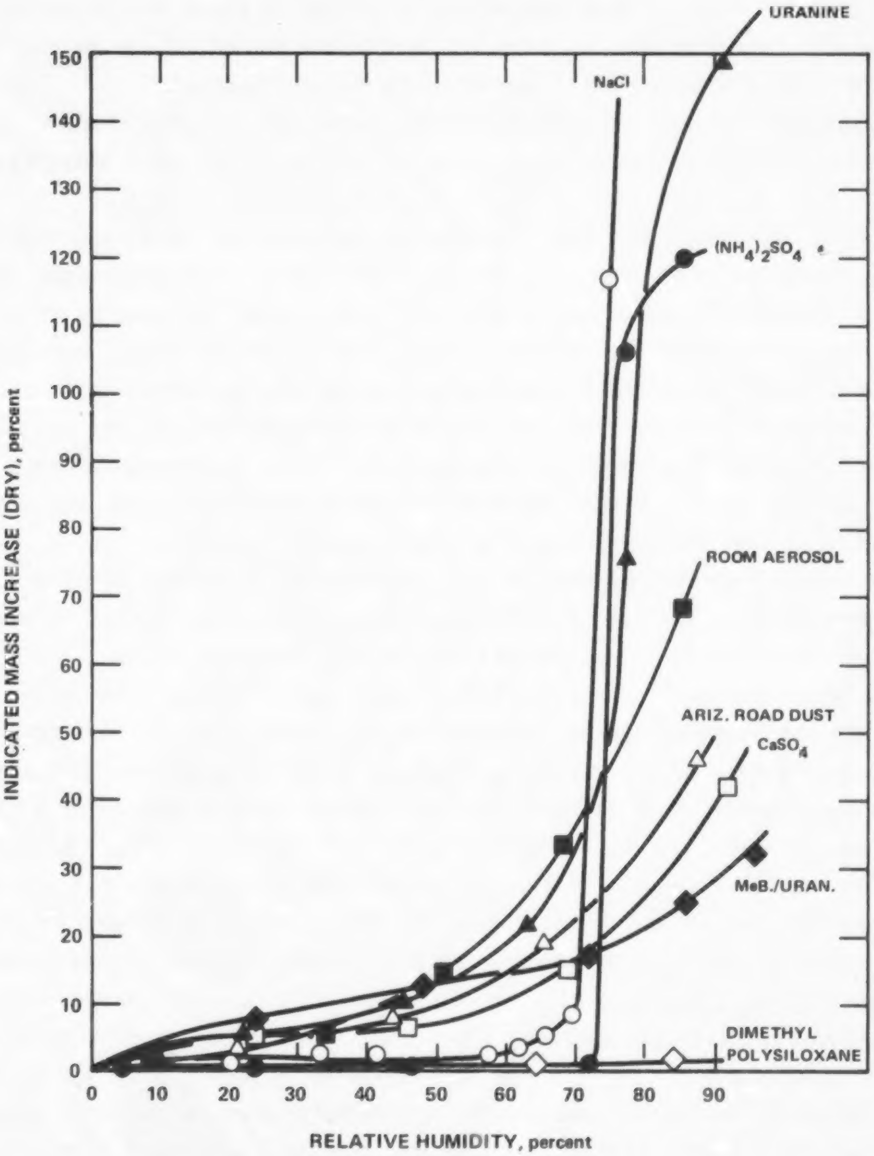

Figure 3-19. Response of a Piezoelectric Microbalance to relative humidity for various particle types.

Source: Lundgren et al. (1976).

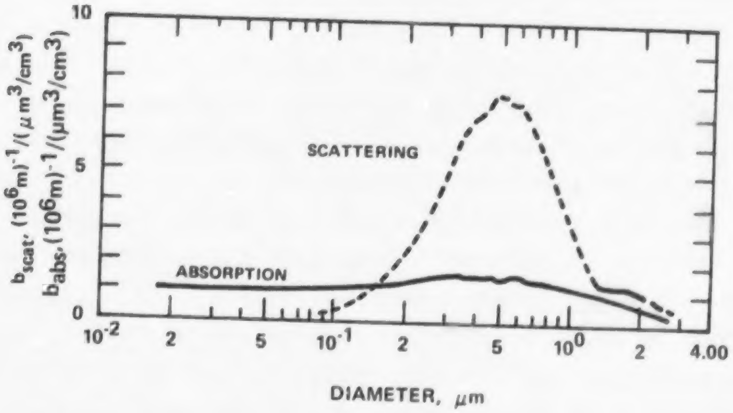

Figure 3-20 Light scattering and absorption expressed per unit volume of aerosol.

Source: Charlson et al. (1978).

3.3.3.2.3 Electrical aerosol analyzer (EAA). The electrical aerosol analyzer, as described by Whitby and Clark (1966), measures the electrical mobility of particles as related to their size. This device provides a detailed number size distribution over the range of 0.01 to 0.5 µm, approximately (Liu and Pui, 1975). The analyzer must be empirically calibrated to obtain the relationship to aerodynamically sized particles. The size range sampled does not include the entire 0 to 2.5 µm fine fraction and comparision between the measurements must include extrapolations.

3.3.3.2.4 Diffusion battery. The diffusion battery, as described by Sinclair et al. (1979), is a set of parallel tubes or plates through which the airstream flows to produce selected differential particle removal as a function of particle size by diffusion to the walls. A condensation nuclei counter is used as the particle counter. This diffusion separation principle is useful in the 0.01 to 0.3 µm range.

3.3.3.2.5 Optical particle counters. Optical particle counters direct the flow stream through a small nozzle into a narrow collimated light beam so that the light scatter from single particles can be measured. The signal produced by this scatter is mathematically related to the geometric size of a spherical particle of a specified refractive index which scatters an equal amount of light. These devices are sensitive to geometric particle diameters from about 0.5 to 10 µm (Whitby and Willeke, 1979). Calibration with monodispersed particles is required. For sampling of particles larger than 10 µm, modification of commercially available devices is required. Mass concentrations for specific size ranges can be estimated by selecting an appropriate particle density. These devices can be used for routine operations, but their usefulness in estimating mass concentrations is limited by the accuracy and consistency of the selected average particle density and index of refraction.

3.3.3.2.6 Long path optical measurement. Long path (typically >1 km) optical measurement devices for ambient air are available. They examine one of several possible aspects of visibility over a defined distance. Transmissometers measure the attenuation of transmitted light resulting from scattering and absorption in the atmosphere. These devices are similar to their in-stack counterparts, requiring either a light source and receptor or light source, retro-reflector, and receptor at separate locations. Telephotometers measure the contrast caused by brightness differences between a distant object and its surroundings. These devices appear to have promise as visibility monitors (see Chapter 9), but estimates of ambient mass concentration have not been made from their data.

3.3.4 Particle Composition

Particles collected from ambient air contain a wide range of metallic elements and inorganic and organic compounds. Their identification and determination usually involves the collection of the particles upon a substrate (e.g., glass fiber filters in a high-volume sampler) with subsequent chemical analysis in a laboratory. Most methods for analyzing the inorganic fraction of particulate matter have focused on elemental and ionic composition. Atomic absorption spectrometry has been the technique most used for the determination of metallic elements, although multielement analytical tools, such as optical emission spectroscopy, X-ray fluorescence spectroscopy, and neutron activation analysis, have been successfully applied to the analysis of elements. For the most part, inorganic ionic species (e.g., NH_4^+, SO_4^{-2}, NO_3^-, etc.) have been analyzed with wet-chemical spectrophotometric techniques. The organic fraction of PM contains aliphatic and aromatic hydrocarbons, acids, bases, and other organic compounds, such as those containing nitrogen. Methods for analyzing organics generally involve solvent extraction, some form of chromatographic separation and detection based on a selected physical or chemical property of the specific compound.

Due to the complex chemical composition of the atmospheric particles and the wide variety of compounds likely to be present, it is not practical to review all the possible methods for their analysis and characterization. Only methods pertinent to the primary objectives of this document are reviewed here in detail. Primary emphasis is placed on methodology for measuring particulate sulfur compounds with lesser emphasis on metallic elements and other inorganic ionic species. Detailed information concerning the analysis of airborne particles is contained in a recent monograph edited by H. Malissa (1978), among others.

3.3.4.1 Analysis of Sulfates--Analytical techniques for determining trace amounts of sulfates in clean, uncomplicated solution matrices are numerous (Forrest and Newman, 1973). However, application of these techniques to complex atmospheric particles is not so straightforward. Quantitative transfer from the collection medium and homogeneous dispersion in the analysis medium--without contamination, chemical alteration, or cotransfer of analytical interferents--is required.

A detailed critical review of the state of analytical methodologies for aerosol sulfur compounds has been compiled by Tanner et al. (1978). Tanner's review includes methods for total aerosol sulfur, for total water-soluble sulfates, and for quantitative differentiation of aerosol sulfur compounds of various oxidation states, as well as a definitive review of methods for speciation of aerosol sulfate. Much of the discussion in this section is taken from Tanner's review, with emphasis on the more widely used methodology. Where information is available, a critical assessment of each method's capabilities is provided.

3.3.4.1.1 Total water-soluble sulfates. A comprehensive review of wet chemical methods has been compiled by Hoffer and Kothny (1974), providing background information on the principal methods for determinating trace sulfates in aqueous extracts of particulate matter collected on filters. Sulfate measurements made with these methods, particularly when applied to the analysis of samples collected with alkaline filter media, are vulnerable to error due to "artifact sulfate" formation caused by the absorption and subsequent oxidation of ambient SO_2 in the presence of the basic components of the filter media. With the use of common glass fiber filters under normal high-volume sampling conditions, this error has been estimated to range from 0.3 to >3 $\mu g/m^3$ (0.1 to > 1 ppb), depending on the ambient SO_2 levels at the time of sampling (Coutant, 1977; Pierson et al., 1980). This potential error should be considered when assessing data collected using any of the methods for water-soluble sulfates discussed below.

Currently, the methods most widely employed for soluble sulfate determinations are the $BaSO_4$ turbidimetric, methylthymol blue, thorin, and ion exchange chromatographic procedures. These methods have inherent analytical precisions, accuracies, detection limits, linear working ranges, and other operational characteristics which will be discussed in the following sections. Each method has an analytical lower detection limit (LDL) and working range for sulfate in the aqueous extract expressed in μg/ml. The corresponding detection limit and working range of each method for measuring sulfate in air expressed in $\mu g/m^3$ depend upon the analytical LDL and the sample size (volume of air sampled, fraction of filter taken for extraction, etc.). For example, if an analytical technique having a working range of 1 to 10 μg SO_4/ml is used to measure sulfate from a typical hi-vol sample (20.3 cm x 25.4 cm filter, 1.4 m^3/min flow rate, 24-hr sample, 1.9 cm x 20.3 cm strip extracted in 50 ml), the working range for sulfate in air would be 0.3 to 2.9 μg SO_4/m^3. It should be noted that the upper range limit can usually be extended to higher concentrations by dilution of the aqueous extract prior to analysis.

3.3.4.1.1.1 $BaSO_4$ turbidimetry. Sulfate in the aqueous extract from a particulate sample is precipitated by addition of barium chloride. The resulting $BaSO_4$ turbidity is measured spectrophotometrically or nephelometrically and compared to a standard curve prepared by measuring the absorbance of standard solutions of sulfate. Numerous versions and modifications of methods based on this principle appear in the literature (Kolthoff et al., 1969; Technicon Corp., 1959; American Public Health Association, 1971; Appel et al., 1979a). Appel, et al. (1979a) described and evaluated a procedure applicable to the measurement of sulfate in aqueous extracts from 24-hour hi-vol particulate samples. They reported an analytical working range from 10 to 70 μg SO_4/ml (2.9 to 20.3 μg SO_4/m^3 for a typical hi-vol sample), an accuracy within 4 percent, and an average precision of 3.8 percent (coefficent of variation) of the working range. They reported that extract background turbidity and color interfere with the procedure but are minimized by means of blanks. Sulfur compounds converted to sulfate by air oxidation also interfere. The apparatus required for turbidimetric sulfate determination is relatively inexpensive and if proper care is taken, the procedure is capable of producing reliable data.

3.3.4.1.1.2 Methylthymol blue (MTB). A reagent containing equimolar amounts of barium ions and MTB, at a pH of 2.8, is added to the aqueous extract from a particulate sample. Sulfate in the solution is precipitated as $BaSO_4$ and the pH of the solution is raised to 12.4 by addition of NaOH. The remaining barium combines with the anionic MTB and leaves an amount of free MTB equivalent to the sulfate. The MTB is measured spectrophotometrically at 460 nm and compared to a standard curve of absorbance versus concentration. Lazrus et al. (1966) described an automated version of this method and reported that the reagent is oxidized in air when made alkaline, thus limiting the use of the method to a closed system.

An evaluation by Appel et al. (1979a) of automated MTB methods examined two procedures; one covering an analytical range of 0 to 100 μg SO_4/ml developed by Midwest Research Institute (MRI) (Bergman and Sharp, 1979) for EPA and the other covering a range of 0 to 10 μg SO_4/ml developed by Colovos et al. (1976). The results for the MRI procedure indicated a working range of 17 to 90 μg SO_4/ml (5.0 to 26.5 μg SO_4/m^3 for a typical hi-vol sample), an accuracy of 1.06 (mean observed/ theoretical) with an average coefficient of variation of 2.8 percent for analyses of filter strips spiked with known amounts of sulfate. Similarly, the results for the Colovos et al., (1976) procedure indicated a working range of 2 to 10 μg SO_4/ml (0.6 to 2.9 g SO_4/m^3 for a typical hi-vol sample), an accuracy of 0.98 and a precision of 1.3 percent. The samples must be treated with an ion exchange resin to remove metal ions which may also react with MTB. No significant sources of interference were found in this evaluation. The automated versions of the MTB procedure are widely used and are capable of producing reliable results. Large sample loads can be analyzed in relatively short periods of time. The equipment is relatively expensive, but can be used for other analyses.

3.3.4.1.1.3 Thorin. Titrimetric methods for sulfate using barium ion and thorin indicator for visual or spectrophotometric detection of the endpoint are popular (Akiyama, 1957; American Society for Testing and Materials, 1981c; Bakas, 1956; Dubois et al., 1969; Fritz, 1955 and 1957; Menis, 1958; Rayner, 1966). These procedures provide for titration of aqueous sulfate with a solution of barium ion to precipitate barium sulfate ($BaSO_4$). When the sulfate is completely reacted, excess barium complexes with thorin to produce a pink color indicating the endpoint of the titration. The samples must be treated with a cation exchange resin to remove metal ions that also complex with thorin.

A recent modification of this technique by Brosset and Ferm (1978) allows rapid determination of sulfate by employing an automatic pipetting system. Aqueous sulfate extract is treated with a solution containing an amount of barium in excess of the anticipated sulfate and $BaSO_4$ is precipitated. Then, a solution of thorin indicator is added, which combines with the remaining barium to form a colored complex. The absorbance of the solution is measured at 520 nm and compared to a standard curve obtained from sulfate standards. The absorbance of the solution is inversely proportional to the sulfate concentration. This procedure has been evaluated by Appel et al. (1977) who reported an effective working range of 3 to 13 μg SO_4/ml (0.8 to 3.8 μg SO_4/m^3 for a typical hi-vol sample), an accuracy of 1.04 (mean observed/theoretical), and a precision of 5 to 9 percent (coefficient of variation). No significant source of interference is reported, but the samples must be corrected for background turbidity and color. The Brosset modification employs an relatively expensive automatic pipet.

3.3.4.1.1.4 Ion exchange chromatography. The principle of the ion exchange chromatographic technique is described briefly under Section 3.2.2.3.6. Stevens et al. (1978) described the use of this technique for analysis of sulfate as well as other ions. Appel et al. (1979a) evaluated a procedure for sulfate analysis using a system manufactured by Dionex Corp. (1975). This procedure showed a working range of 7 to 130 μg SO_4/ml, an accuracy of 1.08 (mean observed/theoretical), and a precision of 6.2 percent (coefficient of variation). A small interference from nitrate ion was also reported. Apparatus for this procedure is relatively expensive and requires a skilled operator. Nevertheless, the procedure is considered to be reliable and specific. Other ionic species can be determined simultaneously.

3.3.4.1.2 Total aerosol sulfur. Nearly 100 percent of aerosol sulfur mass is present in the form of sulfate (Forrest and Newman, 1973a). This was experimentally demonstrated by Stevens et al. (1978), who also showed that most of the data on air-borne sulfur concentrations can be accurately described as total sulfur calculated as sulfate or total soluble sulfate. X-ray fluorescence is the primary and most practical technique for measuring total aerosol sulfur collected on filters. This technique can be used to analyze many elements besides sulfur. It is nondestructive and can be automated to facilitate the analysis of large numbers of ambient aerosol samples. A particulate sample, collected on an appropriate filter (usually Teflon®) is irradiated with photons (X-rays, gamma rays, etc.), protons, or other charged particles, and the intensity of the fluorescent X-rays induced is measured as a function of wavelength or energy to determine the amounts of the constituent elements present. Qualitative and quantitative analysis can be obtained when the system is properly calibrated. This calibration step is difficult, since few standards of known elemental composition are available in disks of known thickness in an appropriate matrix (Adams and Van Grieken, 1975). However, recent work by Dzubay et al. (1977) has shown that calibration standards can be prepared to an accuracy of ± 5 percent.

The most extensive set of aerosol sulfur data were reported by Stevens et al. (1978) and Loo et al. (1978) using a energy nondispersive X-ray fluorescence spectrometer designed by Goulding and Jaklevic (1973). Stevens et al. (1978) reported sulfur and 18 other elements from dichotomous samplers operated in New York City, New York; Philadelphia, Pennsylvania; Charleston, West Virginia; St. Louis, Missouri; Portland, Oregon; and Glendora, California. Loo et al. (1978) reported sulfur concentrations determined from samples collected over a 2-year period from a network of 10 automated dichotomous samplers operated in and around St. Louis, Missouri, during the Regional Air Pollution Study (RAPS). They reported a detection limit of 0.034 $\mu g/cm^2$ of filter, which corresponds to a concentration value of $<0.1\ \mu g/m^3$ sulfur for a 2-hour sample collected at 50 liters/minute on a 37-mm filter and is adequately sensitive for a 1-hour time discrimination at ambient sulfur levels.

Proton-induced X-ray emission spectroscopy, which has the advantages of lower bremsstrahlung background and focusing properties of the exitation beam, is a useful tool when short-time resolution of ambient sulfur levels is desired (Johansson et al., 1975; Courtney et al., 1978). However, it takes substantially more energy to produce an X-ray with charged particles than with photons, and in some cases vaporization or decomposition of the sample may occur (Shaw and Willis, 1978). A related approach to nondestructive aerosol sulfur analysis based on cyclotron in-beam gamma-ray spectroscopy has been reported by Macias (1977). Gamma rays induced by proton or α-irradiation are detected by a Li-drifted Ge detector and used to determine S and other light elements such as Mg and C in aerosol samples. This technique is less sensitive for S than X-ray emission methods. In spite of the aforementioned limitations, it is clear that these induced X-ray and gamma-ray methods will continue to be important tools for determining total sulfur in large numbers of ambient aerosol samples.

Other techniques that have been applied to the determination of total sulfur in aerosol particles include: (1) electron spectroscopy for chemical analysis (ESCA) (Novakov, 1973; and Novakov et al., 1974); (2) various applications of flame photometric detectors (FPD) (Crider et al., 1969; Kittelson et al., 1978; Huntzicker et al., 1976, 1977, 1978; Tanner et al., 1978, 1980); and, (3) an isotope tracer technique using ^{110}Ag tracer (Forrest and Newman, 1977). ESCA is sensitive to surface composition of samples, which is an advantage for surface-oriented studies but not for ambient aerosol samples whose elemental composition is likely to be heterogeneous. A comparison of ESCA to wet chemical sulfate measurements by Appel et al. (1976) showed agreement only within a factor of two. Direct flame photometry has potential as a sensitive total aerosol sulfur analyzer, but its application is complicated because SO_2 must be removed and the FPD response varies with the chemical form of the aerosol sulfate. Recent work by Huntzicker et al. (1978) and Tanner et al. (1980) has shown that direct flame photometry can not only provide a sensitive total aerosol analysis but, when combined with thermal volatilization, can provide semicontinuous measures of H_2SO_4, ammonium sulfate, and metal sulfates.

3.3.4.1.3 Sulfuric acid determination. Most of the efforts to determine the species composition of sulfate in airborne particles have concentrated on development of a specific analytical method for H_2SO_4 in air. Despite the substantial efforts of several groups, the existence of free aerosol H_2SO_4 in the ambient atmosphere has been unequivocally established in only a few cases. Interference problems and difficulties in sample preservation have contributed markedly to the lack of valid H_2SO_4 measurements. The procedures discussed below have been applied primarily by research analysts, are vulnerable to error both in sampling and analysis, and are not generally applicable to routine monitoring.

Procedures for determining H_2SO_4 and other sulfate species include thermal volatilization and solvent extraction techniques, gas phase ammonia (NH_3) titration, infrared and visible spectrometry, flame photometry, and electron microscopy. The determination of H_2SO_4 by its selective thermal volatilization from filters has been reported by several workers (Scaringelli and Rehme, 1969; Dubois et al., 1969a; Maddalone et al., 1975; Thomas et al, 1976; Leahy et al., 1975). This technique generally suffers from poor H_2SO_4 recoveries, poor reproducibility, and interferences from ammonium sulfate salts. The most successful approach to thermal volatilization of H_2SO_4 in ambient aerosol samples was reported by Mudgett et al. (1974). Aerosol samples are collected on Fluoropore® filters, the H_2SO_4 subsequently volatilized by passage of heated (~150°C), dry N_2 in the reverse direction through the filter and released H_2SO_4 determined with a flame photometric detector. Lamothe and Stevens (1976) reported that laboratory aerosol samples of as little as 0.25 μg H_2SO_4 may be determined with reasonable precision. However, serious difficulties were encountered in removing H_2SO_4 quantitatively in the presence of ammonium bisulfate (NH_4HSO_4). They observed that H_2SO_4 is totally removed at 180°C, but NH_4HSO_4 is also partially volatilized; at 140°C, NH_4HSO_4 is not volatilized but H_2SO_4 is incompletely volatilized.

A solvent extraction procedure to remove collected H_2SO_4 aerosol selectively in the presence of other aerosol sulfates was first reported by Barton and McAdie (1971). They concluded that aerosol collection on Nuclepore® filters, followed by extraction with 2-propanol for subsequent analysis by the chloranilate procedure, was selective for airborne H_2SO_4. Subsequent work by Barton and McAdie (1973) reported reduction of interference by buffer control of the 2-propanol extract and also reported development of an automated instrument for the extraction procedure. Leahy et al. (1975) reported, however, that 2-propanol will also extract NH_4HSO_4 quantitatively and partially extract other bisulfates and that it should not be considered a selective extractant for H_2SO_4. They demonstrated that benzaldehyde is a selective extractant for H_2SO_4 in the presence of bisulfates and sulfates. Subsequent radiochemical experiments (Tanner et al., 1977) with $H_2{}^{35}SO_4$ have established that H_2SO_4 may be reproducibly removed from a variety of filter media (Mitex®, Fluoropore®, H_3PO_4-treated quartz) with recoveries varying from 75 percent for 10 μg H_2SO_4 samples to 95 percent for 100 μg samples. The selectivity of the benzaldehyde extraction technique has been confirmed in a study by Barrett et al. (1977) employing laboratory aerosol H_2SO_4 samples as low as 5 μg in the presence of bisulfate and sulfate.

As discussed briefly in the previous section, systems for measuring ambient levels of H_2SO_4 and other sulfate aerosols by flame photometry have been developed recently by Huntzicker et al. (1978) and Tanner et al. (1980). A heated denuder for SO_2 removal allows the direct measurement of total sulfate aerosol and selective thermal volatilization allows the discrimination of semicontinuous measurements of H_2SO_4 ammonium sulfates and metal sulfates. Conversion of the H_2SO_4 or the aerosol sulfates to ammonium sulfate $[(NH_4)_2SO_4]$ by addition of NH_3 eliminates the problem of FPD response variations with the chemical form of the aerosol sulfate.

Since atmospheric sulfate can be associated with various cations, the compounds of sulfate can sometimes be inferred by measuring the cation. If the ions in a series of samples are measured and the ammonium (NH_4^+) content is highly correlated with the sulfate content, then it can be inferred that various NH_4^+ salts of H_2SO_4 are probably present. Brosset and Ferm (1978) and Stevens et al. (1978) described a Gran titration procedure for hydrogen ion (H^+) and a procedure using ion selective electrode for NH_4^+ in aqueous extracts of aerosols collected on Teflon® filters. Stevens et al. (1978) applied such techniques to aerosols collected at Research Triangle Park, North Carolina, during the summer of 1977 and 1978 and found a stoichiometric balance between sulfate ion (SO_4^{++}) and the sum of H^+ and NH_4^+ ion concentrations. The acidity was found to range from none $[(NH_4)_2SO_4]$ to that of NH_4HSO_4.

Dzubay (1979) developed and used a sensitive radiolabeling technique for measurements of acid sulfate aerosols. Liu et al. (1978b) described a new technique that uses an aerosol mobility chromatograph for the detection of sulfuric acid aerosols. Several semiquantitative methods for estimating sulfate species have been investigated. These include gas phase ammonia titration techniques (Dzubay et al., 1974), humidographic techniques (Covert et al., 1980), methods based on infrared spectroscopy (Blanco et al., 1968, 1972; Cunningham et al., 1974; Cunningham and Johnson, 1976), and microscopy techniques (Heard and Wiffen, 1969; Lodge et al., 1960; Frank and Lodge, 1967; Mamane and de Pena, 1978).

3.3.4.1.4 Filter sampling problems related to sulfate analysis. Ideally, the measurement of aerosol sulfate species in PM requires that the sulfate-containing particles from the air be quantitatively collected on a filter surface that does not permit chemical or physical transformations and that does not lead to spurious sulfate particle formation from SO_2 present in the gas stream. The particles must then be transferred to the analysis medium under the same constraints. Sampling for airborne sulfate is especially difficult, since acidic sulfate species react with many common filter materials (e.g., "neutral" glass fiber filters and many plastic filters--Nuclepore®, Acropore®, Millipore®) as well as basic particles in the sample. The result is neutralization of the acid sulfate and alteration of the composition from that extant in ambient air. Many of the historical data on sulfate species are questionable due to insufficient consideration of the above sampling difficulties.

Several filter materials made of Teflon®, have been found to be inert and suitable for nonreactive collection of aerosols, including acid sulfates. The most widely used are backed Teflon® membranes, Fluoropore®, and Mitex®. A modified quartz filter material has been developed (Tanner et al., 1977) from which impurities are removed by preheating to 750°C, and reactive basic sites are removed by treatment with hot, concentrated phosphoric acid. After rinsing and drying, the quartz filters may be used for high-volume, high-efficiency particle collection without interfering with acid determinations of the collected particles at the fractional microequivalent level.

Two additional problems have been identified in filter sampling for airborne sulfate analysis. Sulfur dioxide may be converted to sulfate by adsorption on and catalytic oxidation by the filter material (Lee and Wagman, 1966) and/or by previously collected particles (Coffer et al., 1974). Recent studies by Forrest and Newman (1973a) seem to indicate that active catalytic sites on the filter material are the likely culprits. Experiments by Tanner et al. (1978) with high- and low-level SO_2-spiked ambient air passed through preloaded and clean H_3PO_4-treated quartz filters at high and low linear flow velocities failed to find any evidence of artifact sulfate formation for this filter material. This work was confirmed by the work of Pierson and coworkers (1976) from whose data it is clear that the low sodium content of the Pallflex GAO quartz is the probable reason for the negligibly low artifact sulfate formation.

A second problem results from potential neutralization of acidic sulfate particles by NH_3 in the gas stream traversing the filter. Neutralization by NH_3 and oxidation of SO_2 may both be reduced by "diffusion-denuding" the stream of these gases (without removing significant particles), but this is a cumbersome process, especially for high-volume sampling.

The most effective way to reduce particle formation and transformation reactions on the filter is to collect the smallest airborne particle sample that is compatible with available analytical methods. Minimum-quantity sampling also reduces collision-induced interaction of particles on the filter surface and thus real-life chemical inhomogeneities in ambient particles are more likely to be unaffected by the sampling process. The only way to eliminate confounding interparticle interactions on filters totally is to determine the sulfate in situ without filter collection.

3.3.4.2 Ammonium and Gaseous Ammonia Determination--Gaseous NH_3 and ammonium ion (NH_4^+) measurements are important in understanding speciation of sulfate in airborne particles. Ambient ammonia is by far the most important neutralizing agent for acid sulfate; its concentration is directly related to the chemical form of sulfate in the ambient air. Measurements of ammonia along with the set of species which, by mutual interaction, determine the chemical form of sulfate, are crucial to understanding such pervasive problems as acid rain, visibility degradation and the effects of dry deposition. Ammonium ion is found predominantly in the optical-scattering size range or below and is presumed to be secondary in origin, being formed in the neutralization of acidic sulfate particles. The high correlation of NH_4^+ content with soluble sulfate, in both urban (Tanner et al., 1977a) and rural (Tanner et al., 1977) aerosol samples, and the identification by X-ray diffraction of $(NH_4)_2SO_4$ in dried aqueous extracts of airborne particles would tend to confirm the above hypothesis (Brosset et al., 1975).

Ammonium ion in particulate matter is almost always determined by collection on filters, extraction into an appropriate leach solution, and determination by one of two methods. The first is a concentration measurement by an ion-selective electrode sensitive to either NH_4^+ (Beckman electrode) or NH_3 (Orion or Markson electrodes). The limit of detection is determined by the equilibration time of the electrode, a representative value being 5 to 7 minutes for 20 ppb NH_4^+ concentration in water (Eagan and DuBois, 1974; Gilbert and Clay, 1973). This is marginally sensitive for high-volume samples of rural ambient air where NH_4^+ may be as low as 0.3 $\mu g/m^3$. A later development, the air gap electrode (Ruzicka and Hansen, 1974; and Ruzicka et al., 1974), eliminates the problems of electrode contamination by sensing of the NH_3-water equilibrium across an air gap between the analyte solution and the electrode surface.

The second commonly used method for NH_4^+ traces in aqueous solution is the indophenol colorimetric method based on the color-producing reaction of phenol and hypochlorite in the presence of NH_3. Modifications most analytically useful for determination of NH_4^+ in aqueous leaches were reported by Bolleter et al. (1961) and by Tetlow and Wilson (1964). Automated procedures have been proposed by Lazrus et al. (1968) and by Keay and Menage (1970). The latter method is capable of a lower detection limit of 0.05 μg/ml (as nitrogen), requires only a few minutes of analysis time, and has a minimum sample volume of 2 ml.

Methods for determination of free atmospheric NH_3 can be divided into direct methods and methods in which NH_3 is first immobilized on acid-treated filters, leached, and determined as NH_4^+ by one of the methods described above. Ammonia has been analyzed directly by quantitative conversion to nitric oxide (NO) over a hot catalyst and determination by chemiluminescence of the NO (Hodgeson et al., 1971. and Baumgardner et al., 1979). This method is marginally sensitive enough for ambient levels of NH_3 (limit of detection = ~ 1 $\mu g/m^3$) and must be carefully zeroed in the NH_3 scrubber mode to eliminate interference from atmospheric oxides of nitrogen (NO_x). Filter pack methods using either $KHSO_4$ (Eggleton and Atkins, 1972) or oxalic acid impregnants have been used to collect ambient levels of NH_3, but they are fraught with blank and contamination problems and may not collect ambient levels of 0.5 to 5 ppb NH_3 with reproducible efficiency under commonly observed conditions of temperature and relative humidity. Shendrikar and Lodge (1975) applied the ring oven technique to the determination of ammonia collected from ambient air on filter tapes impregnated with ethanolic oxalic acid. The range for quantitative determination is reported to be 0.1 to 1.00 μg of ammonia.

It has also been proposed that gaseous NH_3 could be determined at or below ambient levels by gas phase reaction with HCl vapor. The resultant ammonium chloride (NH_4Cl) aerosol particles would be measured by a condensation nuclei counter (CNC). Unfortunately, there are several difficulties that severely limit the usefulness of this technique. The concentration of HCl and the relative humidity must be carefully controlled to attain proportionality between number of particles and NH_3 concentration. In addition, it is necessary to provide an ionization source (a corona discharge or a UV light source) in the airstream just prior to HCl vapor addition in order to approximate precise, proportional CNC response. However, this method has potential for extremely high sensitivity and real time operation. McClenny and Bennett (1980) developed a semi-real time detection technique for ambient NH_3 based on integrative collection on Teflon® beads, followed by thermal desorption and detection by either chemiluminescence or photoacoustics. Ferm (1979) and Braman and Shelley (1980) reported collection of NH_3 on diffusion tubes. Ferm used oxalic acid as a coating which is rinsed from the tube at the end of a 24-hour run and analyzed for NH_4^+ by ion selective electrode techniques. Braman and Shelley used a tungsten oxide coating for 20 minute samples and released the NH_3 into a chemiluminescence analyzer by thermal desorption. Hoell, et al. (1980) determined vertical concentration profiles by interpretation of infrared solar spectra obtained with a heterodyne radiometer. Abbas and Tanner (1981) reported work on the continuous determination of gaseous NH_3 using fluorescence derivatization. These recent advances in the development of new techniques for measuring NH_3 will be helpful in determining the role of NH_3 in conversion of H_2SO_4 to less harmful materials.

3.3.4.3 Analysis of Nitrates--Nitrate analyses have been performed routinely for many years, and a large number of chemical methods have been reported. In typical monitoring for nitrate in air, a portion of a particulate filter is subjected to aqueous extraction and the water-soluble nitrate is analyzed by one of the methods discussed below.

3.3.4.3.1 Measurement techniques for nitrates. The oldest procedures for analyzing nitrate used brucine (Intersociety Committee, 1977b) or phenol disulfonic acid (Intersociety Committee, 1977c). Many other methods for analyzing nitrates have been reported, including: (1) the nitration of chromotropic acid (West and Ramachandran, 1966) and coumarin analogs (Laby and Morton, 1966; Skujins, 1964); (2) the quenching of the fluorescence after nitration of fluorescein (Axelrod et al. 1970); (3) reduction with Devarda alloy to ammonia (Kieselbach, 1944; Richardson, 1938); and (4) the use of ion-selective electrodes (DiMartini, 1970; Driscoll et al., 1972; Gordievskii et al., 1972). Microscopic techniques also allow identification and size estimation of individual nitrate particles (Bigg et al., 1974).

One of the most extensively used techniques to analyze nitrates in atmospheric particulate extracts involves reduction of the nitrate to nitrite by zinc (Chow and Johnstone, 1962), cadmium (Morris and Riley, 1963; Strickland and Parsons, 1972; Wood et al., 1967), or hydrazine (Mullin and Riley, 1955). Measurement of the nitrite produced is accomplished by a sensitive diazotization-coupling reaction (Saltzman, 1954). Automated versions of this technique provide much better results because critical reduction parameters such as temperature, surface contact area, and reaction time can be precisely controlled (Technicon, 1973). Lazrus et al. (1968) used an automated system, in which nitrate was reduced to ammonium and determined by the indophenol method. Another extensively used technique to analyze nitrate in atmospheric particulate matter extracts involves the nitration of xylenols and separation of the nitro-derivative by extraction or distillation. A comparison of a 2,4-xylenol procedure (Intersociety Committee, 1977d) with the automated copper-cadium reduction and diazotization method in samples collected near high density vehicular traffic, demonstrated a negative interference in the former up to a factor of 3 (Appel et al. 1977a).

Small et al. (1975) report an application of ion exchange chromatography to the measurement of a wide variety of cations and anions including the nitrate and nitrite ions. The novel feature of this method is the use of a second ion exchange "suppressor" column (after a conventional separating column) that effectively eliminates the ions of the eluting medium. Since the chromatographically separated species of interest leave the suppressor column in a background of deionized water, concentration determinations may be made by a simple and sensitive conductometric technique. Mulik et al. (1976) report the application of this technique to measurement of water-soluble nitrate on hi-vol filters. The separator column, containing a strong basic resin, separates anions in a background of carbonate eluant. The suppressor column, containing a strong acid resin, converts the sample ion and the carbonate eluant to nitric and carbonic acid, respectively. Since carbonic acid has low conductivity and partially decomposes to carbon dioxide and H_2O, the nitrate ion alone is effectively measured in a conductivity detector. Under the experimental conditions, sensitivity of 0.1 μg/ml was reported. The relative standard deviation was 1 percent (95-percent confidence level) for 10 replicate injections at the 5 μg/ml level. At this concentration, no interferences were found from fluoride, chloride, nitrite, sulfite, sulfate, silicate, or carbonate. Positive interferences were found for bromide and phosphate, but the authors suggest techniques for eliminating these.

In other work, Glover and Hoffsommer (1974) and Ross et al. (1975) reported a technique for assay of aqueous nitrate and nitrite extractions by conversion to nitrobenzene. Both techniques involve the nitration of benzene in the presence of H_2SO_4 to form nitrobenzene, a relatively stable compound, followed by gas chromatographic analysis. Careful calibration is required in both procedures, since a significant fraction of the nitrobenzene formed may be lost to the acid layer. Ross et al. (1975) recommended a calibration procedure, whereby a standard is subjected to the same procedures as the unknown, while Glover and Hoffsommer used internal calibration with added nitrotoluene. The lower detection limits reported by Ross et al. (1975) are in the range of 10^{-12}g nitrobenzene in a 1 μl sample. Conversion efficiences for KNO_3, KNO_2, and HNO_3 were reported as 90.3 ± 7.9, 100.4 ± 4.2, and 99.9 ± 5.2 percent, respectively. Glover and Hoffsommer report similar recovery rates for KNO_3 and KNO_2.

3.3.4.3.2 Filter sampling problems related to nitrate analysis. Serious difficulties have been reported to be associated with the routine analysis of nitrates in PM collected using glass fiber filters. In a study of nitrate in auto exhaust, Pierson et al. (1976) reported that glass fiber filters collected about twice as much nitrate as quartz fiber filters. Nitrate also was found on glass fiber filters that were inserted downstream of either quartz or glass fiber primary filters, providing additional evidence of artifact formation from gaseous constituents. Spicer (1976) reported that glass fiber filters completely removed gaseous nitric acid (HNO_3) in low concentrations in gas streams, while Teflon® and quartz filters showed no corresponding effect. O'Brien et al. (1974) described very unusual particle size distribution determinations for photochemical aerosol collected in the Los Angeles Basin. This study used a cascade impactor, and all particle size fractions were collected on glass fiber filters. The authors speculated that conversion of gaseous nitrate precursors on the filter masked the true nitrate size distribution. Okita et al. (1976) reported that untreated glass fiber filters collect nitric acid vapor with a highly variable collection efficiency (0 to 56 percent), suggesting erratic nitrate artifact formation in urban atmospheres containing HNO_3.

In an intensive laboratory investigation of interferences in atmospheric particulate nitrate sampling, Spicer et al. (1978) concluded that all five types of glass filters investigated exhibited serious artifact formation due to collection of gaseous HNO_3 and, to a small extent, NO_2 as nitrate. Cellulose acetate and nylon filters were also reported to collect HNO_3. Negligible interferences were reported for polycarbonate and Teflon® filters. Collection of NO_2 on quartz fiber filters varied with the filter type, with ADL Microquartz showing the least effect. Artifact nitrate formed on the Gelman AE filter was calculated to be less than 2 μg/m^3 during a standard 24-hour hi-vol measurement. This estimate was derived from drawing air samples of about 1 m^3 containing 4512 $\mu g/m^3$ (2.4 ppm) NO_2 through the filters. The relative humidity was 30 ± 10 percent.

Spicer and Schumacher (1977) also reported the results of a comparison of nitrate concentrations in samples collected on various filter types in Upland, California, during October and November 1976. During the experiment, meteorological conditions varied from warm and hazy to hot, dry, very clean desert wind conditions. Nitrate analyses were performed by ion exchange chromatography. All filter types used had comparable particle collection efficiencies according to the manufacturers' specifications. The ratio of nitrate collected on glass fiber filters to that collected simultaneously with identical hi-vol samplers on quartz filters ranged from 2.8 to 49.

More recently, Appel and coworkers (1979, 1980) conducted several studies bearing on both positive artifact formation and loss of nitrate from a variety of filter media. They concluded that gaseous HNO_3 is the principal source of artifact nitrate formation; NO_2 collection only became substantial at high ozone levels. Ambient particulate nitrate values (at San José and Los Alamitos, California) differed by up to a factor of 2.4 depending upon filter medium and sampling rate, in contrast to the much larger differences reported by Spicer and Schumacher, 1977. They also reported that at low HNO_3 levels, nitrate on glass filters indicated (within 3 percent) total nitrate, (i.e., particulate nitrate plus HNO_3 rather than particulate nitrate alone). They concluded that the degree of error associated with glass fiber filter media could be expected to vary with location, time of year, and time of day, paralleling changes in HNO_3 levels.

Laboratory studies by Harker et al. (1977) and ambient studies by Pierson et al. (1980) have suggested that reaction of particulate nitrates with acidic particulate sulfates (e.g., H_2SO_4) can result in negative errors in the determination of nitrate on filters. Formation and subsequent loss of gaseous HNO_3 was presumed to be the mechanism. Recent studies by Appel and Tokiwa (1980) support these observations and indicate that atmospheric particulate nitrate levels obtained with Teflon® filters may be only a small fraction of the true values. Similar studies with Gelman A glass fiber filters showed insignificant nitrate losses.

Another mechanism for the loss of nitrate from particulate samples collected on inert filters is the dissociation of NH_4NO_3 and loss of the resulting HNO_3. The equilibrium vapor pressures of NH_3 and HNO_3 above solid NH_4NO_3 are appreciable and very sensitive to temperature (Stelson et al., 1979). In a laboratory study, Appel et al. (1980) observed losses of up to 50 percent of the particulate nitrate when NH_3- and HNO_3-free air was passed through Teflon® filters loaded with about 200 μg NH_4NO_3 (<0.5 μm particle size) at 20 liter/minute for 6 hours. These results suggest that the volatilization of NH_4NO_3 can be a major source of negative error in sampling particulate nitrate with Teflon® filters. The presence of relatively high NH_3 and HNO_3 levels in ambient air or high humidity may decrease the error, while elevated temperatures should increase it.

These results point to the conclusion that most of the existing data on urban ambient nitrate concentrations are of doubtful validity. Furthermore, it is unlikely that any of these data can be corrected even if mechanisms for artifact formation or nitrate loss are clarified in the future, since HNO_3, which appears to play a significant role in each mechanism, is not routinely monitored.

3.3.4.4 Analysis of Trace Elements--Over the years, a variety of techniques have been applied to analysis for elements. Presently, the most commonly used techniques use some type of spectroscopic detection. By definition, these techniques respond only to the presence of the elements in the PM and do not provide information concerning the chemical compounds present. For the most part, techniques for analyzing trace elements have not provided information concerning the oxidation state of the elements, although Braman et al. (1977) reported attempts at such analysis for arsenic.

3.3.4.4.1 Atomic absorption spectrometry. Atomic absorption spectrometry (Morrison, 1965) has been widely employed for quantitative analysis of a large number of elements in particles. In principle, a beam of light of a wavelength that is characteristic of an electronic transition for the element of interest is made to traverse a region of space with a constant intensity and to impinge on a detector. The element of interest is atomized in a portion of the beam of light. The amount of light absorbed by the atoms of interest in the sample can be related to the amount of that element present. Any element can be determined if a lamp is available to produce the characteristic light.

A variety of techniques can be used for atomizing and introducing the element into the light beam. Generally, a flame or a heated carbon rod atomizer is used. Flame techniques are most commonly used for atmospheric PM. An extract of the PM is prepared and aspirated into the flame, which volatilizes the sample and produces a sufficiently large population of ground state atoms for absorption. An example of this kind of application is the EPA reference method for lead (U.S. Environmental Protection Agency, 1979d). If the concentration of the element of interest is too low for flame application, however, or if an extremely limited amount of sample is available, an electrically heated atomizer can be used to volatilize atoms into the light beam. In this application, solutions can be used, or a small portion of soiled filter without any other preparation may be examined directly. In the latter case the filter substrate must be oxidizable and the representativeness of the sample may be questioned.

Properly applied, atomic absorption spectrometry is generally specific for the analysis of the elements desired. The instrumentation can be inexpensive relative to other instrumental techniques for the analysis of trace elements and is generally available as standard equipment in most analytical laboratories. However, it can only analyze one element at a time. Additional elements must be determined serially. This can be a severe disadvantage when a number of elements need to be determined on the same sample, both from the standpoint of the resources required to obtain the information and the limitations of the volume of extract available to perform the analysis. Although the technique is useful, there are significant interference problems in some determinations. Spectral interferences from other elements absorbing at the same wavelength can be a problem but can usually be avoided by judicious choice of wavelengths. However, interference effects on the element of interest caused by other substances present in the material introduced into the spectrometer, refered to as matrix effects, can be much more difficult to resolve. These effects can differ significantly, ranging from the effect of viscosity on the amount of material which can be atomized to effects due to the presence of refractory compounds containing the element of interest, which may not be completely volatilized at the flame or atomizer temperature. Matrix effects can adversely affect the concentration of atoms in the beam and result in significant errors in the measurement of an element. The literature is replete with discussions of these difficulties and provides both general and specific techniques for overcoming them. One of the more convenient ways to keep abreast of developments in this area is through the use of a continually updated bibliography with convenient indexing, such as that provided by "Atomic Spectroscopy." (S. Slavin, ed.) Bibliographies for this publication are routinely updated and appear each January and July.

3.3.4.4.2 Optical emission spectrometry. Optical emission spectrometry is a technique which can simultaneously determine the amounts of numerous elements. The advantage of this technique are obvious in situations of limited sample availability or limited time and resources with which to do a measurement. Conventional arc or spark-excited optical emission spectrometry has been used extensively on atmospheric PM (Scott et al., 1976). In most applications of this technique an extract of the PM is excited by a spark or arc discharge. This decomposes any substances present and excites the atoms to other than their ground electronic states. In the de-excitation to the ground state, light is emitted at a characteristic wavelength. The intensity of the light emitted is an indication of the quantity of the element present. Most conventional optical emission spectrometers are capable of simultaneously analyzing 20 to 30 elements.

Conventional arc or spark-excited optical emission spectrometers were never very popular, partly because of cost, partly because the photographic readout was complicated and gave rather approximate answers, and partly because of high detection limits for a number of species. The development of optical emission spectrometers based on plasma excitation (Boumans and DeBoer, 1975) has resulted in significant improvements. Although there are several kinds of plasma excitation, the commercially available optical emission spectrometers with inductively coupled argon plasma excitation has proven most advantageous. In this technique, an extract of the sample of PM is aspirated into an inductively coupled argon plasma whose very high temperature decomposes the materials and excites the atoms. The light emitted when these excited species fall back to the ground state is collected and monitored just as before. However, this approach has numerous advantages not available with the older excitation techniques. The technique is capable of using the same acid extract used in atomic absorption. It is more free of matrix effects than atomic absorption; it requires, for a single multielement determination on a given sample, about the same amount of time and solution as a single element determination on atomic absorption; it usually has a much wider linear range than atomic absorption; and it has detection limits equal to or lower than flame atomic absorption (Fassel, 1978). If an acid extract of atmospheric PM is to be analyzed, inductively coupled argon plasma optical emission spectrometry is usually the technique of current choice.

3.3.4.4.3 Spark source mass spectrometry. Spark source mass spectrometers are high-resolution magnetic sectoring mass spectrometers which usually use photographic emulsion detection and very high resolution densitometry for quantitative analysis. They are uncommon and very expensive. The material to be analyzed is incorporated into two small (usually graphite) electrodes, which are placed in the spectrometer with a well-controlled gap between them. A spark is passed across the electrodes, vaporizing them and ionizing the material in them. The ions are subsequently led into the mass analyzer portion of the spectrometer (Ahern, 1972).

The electrodes used in the spark source mass spectrometer can be fabricated either from PM that has been separated from a filter or an extract of the PM. The technique is not suitable for the generation of large data bases because only a few samples can be analyzed on any given day. The time required to prepare the instrument and to obtain a set of spectra necessary for quantitation is substantial. Double ionization of elements is common and so are ionized oligomers of carbon. Therefore, high resolution detection and complex interpretation are the rule rather than the exception. The advantage of spark source mass spectrometry is that it can simultaneously estimate the quantity of all nonvolatile elements in the periodic table and can do so with roughly equal sensitivity.

3.3.4.4.4 Neutron activation analysis. Neutron activation analysis (Morrison, 1965) implies a variety of distinct procedures, all of which produce unstable atomic nuclei which then emit high-energy radiation or particles. The intensity of a specific emission and its energy are monitored as an indicator of the element and its quantity.

Instrumental thermal neutron activation analysis is the technique most commonly applied to atmospheric PM. With this approach, a nuclear reactor is used to produce neutrons, which bombard the samples and produce the unstable nuclei. The emitted gamma radiation is detected by a Li-drifted Ge detector whose output is processed to produce the gamma-ray spectrum of the irradiated PM. The method has low detection limits, can simultaneously determine up to about 25 elements in a given sample, and particulate matter can be analyzed directly as received on a very small portion of the filter surface. The technique has been successfully applied with the glass fiber used in hi-vol samplers (Lambert et al., 1979). The time required for analysis is short. However, data are usually not available until 2 to 3 weeks after the sample is irradiated because there is a significant delay period between the irradiation and the collection of gamma-ray spectra for certain long-lived isotopes. Some important elements (e.g., S and Pb) are not practically measured using this method. These limitations and the need for very complex, highly specialized and expensive equipment are the main disadvantages of the neutron activation technique.

3.3.4.4.5 X-ray fluorescence spectrometry. X-ray fluorescence spectrometry is a multi-element, nondestructive technique that can simultaneously determine numerous trace elements in PM, directly on the filter media. It involves the excitation of tightly bound electrons in the atoms by an X-ray generator and observation of the X-ray emissions that occur as the de-excitation of the electrons proceeds (Dzubay, 1977).

X-ray fluorescence spectrometers use either energy-dispersive or wavelength-dispersive detection. Spectrometers using energy-dispersive detection simultaneously collect all emitted quanta with a silicon-lithium detector and, through subsequent processing, can analyze about 30 elements. Spectrometers using wavelength-dispersive detection monitor carefully preselected wavelengths that are characteristic of the de-excitation emissions of the elements of interest. With wavelength-dispersive detection, about 20 elements can be determined simultaneously on a single sample and interelement effects are minimal due to the high resolution capability of the instrumentation. With energy-dispersive detection, all wavelengths are simultaneously collected and interelement corrections must be handled in the data reduction process.

Good detection limits and the ability to handle a sizable number of samples nondestructively with minimal sample preparation are clear advantages of the X-ray fluorescence technique. In order to analyze the sample directly, however, it must be of uniform surface texture, and it is best if the particulate layer is very thin. This obviously places some limitations on the kind of sample that can be analyzed without preparation. Even in the most ideal samples, concern with special corrections must exist (Gould et al., 1976). The techniques has been applied extensively to analysis of filters from dichotomous samplers (Dzubay and Stevens, 1975).

3.3.4.4.6 Electrochemical Methods. Electrochemical methods have been used to a limited extent to determine a small number of elements in airborne particles. These methods include potentiometry with ion selective electrodes, polarography, and anodic stripping voltammetry (Morrison, 1965). Electrochemical techniques have few advantages for airborne particulate analysis, aside from their low initial capital equipment cost compared to other techniques. While the methods are usable (Ryan and Siemer, 1976) there appears to be fairly little use of such techniques at present, except in the area of ion-selective electrodes.

3.3.4.4.7 Chemical methods--In the past, many classical wet chemical procedures were employed for trace element analysis of airborne particles. In general, a color-forming reagent was involved. The amount of the given element present is determined by the extent of color development. Perhaps the best known of these procedures is based on the use of diphenylthiocarbazone (dithizone) as the colorimetric reagent for lead (Snell, 1978). Wet chemical procedures are labor intensive and slow compared with spectral techniques. Sample preparation and interferences are also usually a problem. As a result, laboratories with heavy sample loads tend to use instrumental methods, particularly spectral techniques.

3.3.4.5 Analysis of Organic Compounds--Numerous papers have appeared dealing with the characterization of organic compounds in airborne particles. The following discussion was taken primarily from the monograph edited by H. Malissa (1978) and describes the principal methods used in this field and some typical examples mentioned in the literature.

Organic compounds significantly contribute to total PM in urban aerosols. Organic contents of up to 43 percent of the total particle mass have been reported (Hidy, 1975). Characterization of organic compounds in urban aerosols generally involves trace separation and identification by gas and liquid chromatography, with detection methods having sensitivity in the nanogram range. The sample amount needed to allow analysis of substances in parts per million concentrations is in the milligram range (Cautreels and Van Cauwenberghe, 1976; Ketseridis, et al., 1976). Usually, high-volume samplers with glass fiber filters are used to provide the needed sample sizes.

One of the earlier simple and extensively used methods for estimating the organic content of PM was called "benzene soluble organics." Filters were simply refluxed with benzene in a soxhlet extractor for several hours. The benzene was evaporated, and the weight of the residue was measured and reported. Benzene soluble organic data were recorded in the National Aerometric Data Bank for many years. Because of the purported hazard of benzene, this method has not been used on a national scale by any single laboratory for roughly a decade. Extraction efficiencies of 25 different solvents and 24 binary mixtures were investigated by Grosjean (1975). Grosjean determined that extraction with benzene or other nonpolar solvents usually leads to serious underestimation of aerosol organics, especially of the polar secondary (photochemical) products like carbonyl compounds, organic nitrates, or carboxylic acids. The use of binary mixtures for extraction or a nonpolar and a polar solvent for successive extractions was strongly recommended. This leads to a higher organic carbon extraction efficiency (in comparison to benzene as solvent) than with both single polar and nonpolar solvents.

In the area of compound-specific analysis, a large amount of early work techniques focused on the measurement of polycyclic aromatic hydrocarbons (PAH). Numerous measurement techniques have been proposed to analyze quantitatively for many of the polycyclic aromatics. Chromatographic techniques (Sawicki, 1964; Thomas et al., 1960) were used in much of the earlier work; more recently, frozen solution fluorimetry (Bacon et al., 1978) and matrix isolation spectroscopy (Wehry and Mamantov, 1979) have been explored. High-pressure liquid chromatography (HPLC) is a promising technique for separation of high molecular weight PAH. The development of bonded octadecylsilyl (ODS) columns of micro particle size allowed Fox and

Staley (1976) to accomplish the near baseline separation of the benzo[a]pyrene (BaP) and its isomer, benzo[e]pyrene. A significant increase in sensitivity over other methods was achieved by use of fluorescence spectroscopy for on-line detection. Perhaps the most extensive data base has been concerned only with BaP (Swanson et al., 1978) utilizing a thin layer chromatographic technique with fluorescence detection. Gas chromatographic (GC) separation of organic extracts of airborne particles requires the application of preseparation steps, such as thin layer chromatography (Zoccolillo et al., 1972) or liquid-liquid extraction (Cautreels and Van Cauwenberghe, 1976; Ketseridis et al., 1976). Primary extraction is generally carried out by means of single solvents such as benzene, cyclohexane, or others. A typical procedure including solvent extraction for preseparation is described by Ketseridis et al.(1976).

The application of gas chromatography coupled with mass spectrometry for the analysis of benzene-extractable compounds in airborne particles is described in detail by Cautreels and Van Cauwenberghe (1976). This work led to the identification of more than 100 compounds in urban aerosols. The benzene-extractable compounds (5.8 percent of total particles) were separated into neutral, acidic, and basic substances. The acidic fraction was converted to the methylated derivatives for GC analysis. In the neutral fraction, 22 saturated aliphatic hydrocarbons, 36 polynuclear hydrocarbons, and 13 polar oxygenated substances were identified. In the acidic fraction, 19 fatty acids and 19 aromatic carboxylic acids were identified. In the basic fraction, 15 peaks of nitrogen-containing analogs of the PAH were identified.

Interest in the organic content of atmospheric particles ranges from particulate carbon (Rosen and Novakov, 1978) to any other possible organic substance. A variety of techniques have been used in an effort to solve this problem (Fox and Jeffries, 1979). However, it is clear that this area is large, exceedingly complex, and will need a great deal of developmental effort.

3.3.4.6 Analysis of Total Carbon and Elemental Carbon--The most widely used technique for measurement of total carbon in collected PM is by combustion to carbon dioxide followed by detection of this gas; or, after CO_2 to CH_4 reduction, of an equivalent quantity of CH_4. Several commercial instruments are available for this purpose. Johnson and Huntzicker (1979) have designed an instrument for analysis of organic and elemental carbon on filter samples of ambient particles. The organic carbon is volatilized or pyrolyzed in an inert atmosphere, oxidized to CO_2, and converted to methane, which is detected with a flame ionization detector. Elemental carbon is determined after oxidation to CO_2 and chromatographic separation of the CO_2 from O_2. Cadle et al. (1980) have discussed a similar system using non-dispersive infrared detection of the CO_2 and automation of the analysis procedure.

Nondestructive analysis of carbon in collected PM involving the interaction of light with the particles (i.e., changes in reflection, transmission, and absorption of the filter) is used to estimate elemental carbon loading. Delumyea et al. (1980) used a reflectance technique having a tungsten filament lamp as a light source. Lin et al. (1973) described an apparatus to integrate light scattered by particles collected on Nuclepore® filters. Since elemental carbon is the major absorbing species in ambient PM, this technique has been used by other researchers to estimate the elemental carbon content of collected PM. Yasa et al. (1979) have shown a linear relationship between photoacoustic measurements and optical attenuation measurements of the type done by Rosen et al. (1978), to establish that the optically absorbing component of urban aerosol particles is graphitic carbon. Photoacoustic measurements have also been used for in-line measurements of diesel particulate emissions (Faxvog and Roessler, 1979). (See Chapter 9 for a more thorough discussion of the role of light absorbing particles in visibility reduction.)

Macias et al. (1978) used the gamma-ray analysis of light elements (GRALE) technique to measure carbon in ambient aerosols deposited on quartz or Teflon filters. The GRALE technique involves the in-beam measurement of gamma rays emitted from an aerosol sample during the inelastic scattering of 7-MeV protons accelerated in a cyclotron.

Calcium carbonate also is commonly found in airborne particles. Mueller et al. (1971) described a technique to distinguish carbonates from elemental carbon by acid evolution of CO_2.

3.3.5 Particle Morphology Measurements

Visual examination of particles collected on a filter or impaction substrate can provide extremely useful information concerning the sources and transport of airborne particles. A reticle-equipped light microscope can be used to examine particles larger than about 0.5 µm. Use of transmission and scanning electron microscopes can improve the resolution for particles as small as 0.001 µm. The effective ranges of microscopes and their utility are described by McCrone (1973) and shown in Appendix Figure 3A-13. Particle size distributions by number can be generated using statistically valid counting procedures. By applying an average density an estimate of the size distribution by mass can be made.

Microscopic identification and analysis requires a high degree of skill and experience plus extensive quality assurance to provide meaningful information. Critical factors in effective use of these methods are the selection of sampling substrates, allowable particle loadings, and sample handling. In addition, particle interactions and structure changes on the collection surface must be minimized if accurate size distributions and characterizations are to be obtained. In a study of ambient particles collected on hi-vol filters, Bradway et al. (1976) examined the ability of multiple microscopists to characterize particles in specific categories. Significant misidentification and misassignment problems were noted, which made it difficult to compare results. Multiple microscopists and blind replicates were recommended as standard procedures for quantitative optical characterization studies.

3.3.6 Intercomparison of PM Measurements

The intercomparison of particle sampling methods is not straightforward because of the complex nature of ambient particulate matter. As noted earlier in this chapter, gravimetric mass measurement methods can differ dramatically in the particle size ranges collected and the sensitivity of the sampler to external factors, such as windspeed. Also, nongravimetric mass measurement methods examine only specific portions of the particle size spectrum and, in addition, measure selected integral properties of particles rather than mass.

Comparison of gravimetric mass measurement methods can be made in the field through collocated sampling or in the laboratory by examining the sampling effectiveness of the inlet or substage for various particle sizes. Because it is difficult to simulate the character of real suspended particles, however, the final intercomparison test must be performed at selected field locations. The choice of the number and types of field locations is important, since the local particle sources can have a substantial impact on the sampler performance, especially if coarse particles dominate the size distribution.

The most recent and comprehensive intercomparison of gravimetric mass measurement particle samplers was reported by Camp et al. (1978). Eleven different types of samplers were compared for mass and other analyses including sulfates, nitrates, and elemental composition. The most salient observation of the study was the difficulty of intercomparison of the samplers because of differences in inlet or substage particle size cutpoints. Since there is no reference sampler, all measurements of the same size fraction were averaged as a comparison measurement. Some duplicate samplers were present, permitting reproducibility measurements. The coefficient of variation for the automated dichotomous samplers was determined to be 11 percent for the coarse fraction and 3 percent for the fine fraction. The same values for a manual dichotomous sampler were 18 percent and 7 percent, respectively. The high-volume impactor used in the CHAMP network gave values of 15 percent and 5 percent, respectively, for the equivalent size fractions. The results from this study should be considered "best case," since the sampler operations were monitored continuously by highly skilled individuals. In some cases, the operators were the developers of the sampling method. It is expected that routine field sampling by less qualified personnel would produce larger variabilities. The reproducibility of certain chemical analyses were reported to be better than the mass measurements, such as elemental sulfur which averaged ±3 percent for all size fractions. Overall, the study showed that comparable results could be obtained by different particle samplers if appropriate quality assurance steps were taken and identical size fractions were compared.

Miller and DeKoning (1974) compared the TSP high-volume sampler with several commercially available cascade impactors. None of the impactors gave results comparable to the high-volume sampler, but the two types of samplers did correlate reasonabley well. The agreement among cascade impactors for mass median diameter (MMD) was very poor. The MMD often differed by more than a factor of 2.

Comparison of gravimetric mass measurements with indirect mass measurements should only be attempted to determine correlation or to test a physical model relating the measurements. The literature contains many intercomparison studies attempting to relate the TSP hi-vol with surrogate techniques such as: the British Smoke Shade sampler (Commins and Waller, 1967; Lee et al., 1972; Pashel and Egner, 1981); the integrating nephelometer (Charlson et al., 1968; Kretzschmar, 1975); and the AISI tape sampler (Lee et al., 1972; Ingram and Golden, 1973). Comparisons are also available between other direct and indirect mass measurements, such as the dichotomous sampler with the AISI tape sampler (Regan et al, 1979) and with the nephelometer (Waggoner and Weiss, 1980). In many cases, a simple regression was fitted between measurements rather than attempting to establish a physical basis for the comparison for testing with empirical data. Most of these comparisons were attempts to demonstrate the usefulness of a nongravimetric sampling method for predicting the mass concentrations that would have been measured by a gravimetric mass method. However, there is currently no indirect technique that has gained acceptance as a general-purpose surrogate for direct mass concentration measurements.

Mulholland et al. (1980) compared the estimated mass concentrations calculated from Electrical Aerosol Analyzer (EAA) measurements with direct gravimetric analyses. It was noted that the errors are in the ± 20 to 30 percent range for spherical particles, and for nonspherical particles the errors are as high as ± 60 percent. Therefore, great care should be taken in attempting to predict gravimetric mass concentration from nongravimetric particle measurements.

3.3.7 Summary

Particulate matter suspended in ambient air contains a range of particle sizes and shapes. Separating particles according to aerodynamic size groups particles that behave alike in more situations of interest to human health and welfare (other than visibility) than any other measure of particle size. Samplers can be designed to collect specific size fractions or match specific particle deposition patterns through carefully designed inlets and substage fractionators. Mass concentration derived from gravimetric analysis is the most common measure of PM. High-volume samplers, dichotomous samplers, cascade impactors, and cyclone samplers are the most common examples of this type of measurement. Carefully collected size distributions of ambient particle mass have shown that most particle samplers underestimate the concentration of particles in the air because of external factors such as windspeed or because their particle transport systems are not effective for the larger particle sizes.

Mass concentrations can be estimated using methodologies that measure an integral property of particles such as optical reflectance. Empirical relationships between mass concentrations and the integral measurement have been developed and are used to predict mass concentration. Without a valid physical model relating the measurements plus empirical data to demonstrate the model, these techniques have a limited ability to estimate mass concentrations. These conditions are poorly met in the case of reflectance or transmission tape samplers, fairly well met in the integrating nephelometer, and very well met in the case of beta-ray attenuation analysis.

Sampling accuracy is difficult to determine directly, since the measurement requires the production of very accurately known concentrations of particulate matter of a wide variety of sizes. Instead, accuracy is estimated by determining the accuracy of sampler flow rate measurement or control, and inlet sampling effectiveness. These separate measurements provide a means of intercomparing methods in the absence of a reference measurement technique. Recent interest in larger particle sampler cutpoints (e.g., 15 μm) have resulted in wind tunnel test procedures for particles that determine sampling effectiveness under controlled conditions. Such measurements have added significantly to the ability to estimate particle sampling accuracy.

Recent evaluations show that the high-volume sampler collects a smaller particle size range than that reports in the 1969 criteria document (National Air Pollution Control Administration, 1969). The sampling effectiveness of the hi-vol inlet also is wind speed-sensitive for larger (>10 μm) particles. Sampling biases caused by typical wind speeds could be expected to cause no more than a 10-percent day-to-day variability for the same ambient concentration. The hi-vol is one of the most reproducible particle samplers currently in use, with a coefficient of variation of 3 to 5 percent. A significant problem associated with the glass fiber filter used on the hi-vol is the formation of artifact mass caused by the presence of acid gases in the air. These artifacts can add 6 to 7 $\mu g/m^3$ to a 24-hour sample.

The dichotomous sampler was designed to collect the fine and coarse ambient particle fractions, usually providing a separation at 2.5 μm. This sampler uses Teflon® filters to minimize artifact mass formation and is available in versions for manual or automatic field operation. The earlier inlets used with this sampler were very windspeed dependent, but newer versions are much improved. The dichotomous sampler collects submilligram quantities of particles because of low sampling flowrate and requires microbalance analyses, but is capable of reproducibilities of ± 10 percent, or better.

Cyclone samplers with cutpoints in the vicinity of 2 μm have been used for years to separate the fine particle fraction. A recent development has coupled the cyclone sampler to a sampler inlet to give a 15 μm cutpoint. Cyclone samplers can be designed to cover a range of sampling flowrates and are available in a variety of physical sizes. A 10mm version is available for personnel dosimeter sampling. Cyclone sampling systems could be expected to have coefficients of variations similar to that of the dichotomous sampler.

The Size Selective Inlet (SSI) hi-vol collects samples containing particles less than 15 μm for comparison with TSP. This sampler is identical to the TSP hi-vol except for the inlet and is expected to have the same basic characteristics.

Cascade impactors have been used extensively to obtain mass distribution by particle size. Because care must be exercised to prevent errors, such as those caused by particle bounce between stages, these samplers are normally not operated as routine monitors. A comparison of impactors showed inconsistencies in the MMD and in total mass collections compared with the hi-vol.

Samplers that derive mass concentrations using analytical techniques other than direct weight have been used extensively. One of the earliest was the British Smoke Shade sampler, which measures the reflectance of particles collected on a filter and uses empirical relationships to predict mass concentration. These relationships have been shown to be more sensitive to carbon concentrations than mass; hence, they are very difficult to interpret as total mass. Another optical technique, the AISI tape sampler, uses transmittance instead of reflectance to predict mass. It has been shown that this sampler correlates favorably with gravimetric measurements limited to the smaller particle sizes. Several researchers have also reported good correlation between the integrating nephelometer and gravimetric fine particle mass. The EAA, however, was shown to have difficulties in reliably predicting gravimetric mass measurements.

Optical particle morphology techniques are very useful for identifying the character and sources of collected particles. Researchers have noted, however, that these techniques are dependent on the skill of the microscopist and stressed the need for careful quality assurance procedures.

An extensive number of analytical techniques are available for analyzing particles collected on a suitable substrate. Many of the analytical techniques, such as those for elemental sulfur, have been demonstrated to be more precise than the analyses for gravimetric mass concentration. Methods are available to provide reliable analyses for sulfates, nitrates, organic fractions, and elemental composition (e.g., sulfur, lead, silicon). Not all analyses can be performed on all particle samples because of factors such as incompatible substrates and inadequate sample size. Misinterpretation of analytical results can occur when samples have not been appropriately segregated by particle size and when artifact mass is formed on the substrate rather than collected in a particle form. Positive artifacts are particularly likely in sulfate and nitrate determination, and negative nitrate artifacts also occur.

Sampling technology is available to meet specific requirements, such as providing sharp cutpoints, cutpoints which match particle deposition models, separate collection of fine and coarse particles, automated sample collection capability, collection of at least milligram quantities of particles, minimal interaction of the substrate with the collected particles, ability to produce particle size distribution data, low purchase cost, and simple operating procedures. Not all these sampling requirements may be needed for each measurement study. Currently, there is no single sampler which meets all requirements, but samplers are available that can meet most typical requirements.

3.4 MEASUREMENT TECHNIQUES FOR ACIDIC DEPOSITION

3.4.1 Introduction

Studies designed to monitor precipitation first appeared in the literature around the turn of the century. Many small-scale networks were organized in the United States and Europe between the 1920's and the 1950's. Knight (1911), Wilson (1926), and Collison and Mensching (1932) reported the earliest U.S. precipitation chemistry studies at local sites. The physical size of the networks changed during the 1950's from single or dual site studies to large-scale national/international studies. During the 1950's, Barrett and Brodin (1955) organized a European monitoring network and Junge and Gustafson (1956) established the first continental U.S. network. The World Meteorological Organization (WMO) reported (1971) the formation of an international network to monitor global trends and changes in the chemical composition of acid precipitation. In addition to the existing WMO network, various local, regional, and national acid precipitation studies currently operate in the industrialized nations.

Ecologists and biologists were among the first scientists to become concerned with the causes and effects of acid precipitation. These two groups were responsible for most of the acid precipitation studies conducted before 1970. During the period 1974-1976, multidisciplinary study of acidic precipitation phenomena expanded. International scientists from every scientific field focused their attention on the potential affects of acidic precipitation. Symposia, committees, and groups were organized to examine every facet of past and on-going studies (Dochinger and Seliga, 1976; Kronebach, 1975; Likens et al., 1972; Likens, 1976). Network siting, sampling procedures and analysis schemes were critically reviewed. Special committees were formed to develop techniques to describe statistically the quality of the precipitation chemistry data being reported by the various international laboratories. During this period, concern about the effects of particulate deposition on vegetation increased. As a result, improved wet/dry collection devices were designed to give a better understanding of total acidic deposition problems.

Many new studies resulted from this increased emphasis on acidic deposition, including the development of a long-term continental U.S. monitoring network (Galloway and Cowling, 1978). Comprehensive reviews of past and current studies are provided by Niemann et al. (1979); Kennedy (1978); and the U.S. Atomic Energy Commission (1974).

3.4.2 U.S. Precipitation Studies

Past U.S. precipitation chemistry studies can best be described as ad hoc (U.S. Atomic Energy Commission, 1974). New studies were randomly developed without adequate consideration of either past or current proposals. General characteristics of past U.S. studies include:

1. Overall study objectives varied among projects.
2. Pre-1970 studies were short-term, lasting only 1 to 2 years.
3. Sites were randomly selected at locations of convenience. Siting with respect to program objectives or standard siting criteria were rarely considered.
4. Sampling/storage procedures and the extent of sample chemical analysis varied among studies.

Each of these deviations in study design/protocol obviously affects the existing data and precludes any simplistic consolidation or correlation of past study results. Of these variations, the differences in sampling/storage procedures are the most difficult to resolve. In general, sampler collection efficiencies, sample representativeness, and sample integrity at the time of chemical analysis (i.e., does the sample reflect what was collected in the field or have chemical changes occurred?) can only be speculative for the earlier studies.

Since 1900, techniques used to collect and store precipitation samples have changed. The most significant change in wet-only or bulk precipitation sampling is in the collector itself. In earlier reports, monthly bulk samples were manually collected in glass devices. Plastic devices became the collection medium during 1950-1960. Galloway and Likens (1976) note that plastic collectors are preferred today for inorganic species, whereas glass collectors are currently used for organic sampling. Automated wet/dry samplers are replacing the manual wet-only and bulk collection techniques. The height of the collection device above ground level has varied throughout the years. Earlier studies placed collectors at ground level while current studies commonly place the collector 1 to 3 meters above ground level. Other study-dependent sampling variations observed in wet-only and bulk sampling procedures include: filtering versus non-filtering of the sample before chemical analysis; the use of biocides to preserve the sample and retard biological growth; and the storage techniques used after sample collection and before chemical analysis. Although the degree to which each of these sampling and storage differences affect the sample remains unanswered, it is generally agreed that the study data will be related to the study sampling techniques employed.

When reviewing past studies, the extent to which these common variations biased the resulting data must be determined. For example, the effects of sample evaporation, splash contamination, loss of initial (usually most concentrated) rainfall, and contamination from insects, leaves, etc., have been commonly reported. How the authors addressed these problems differ. Some deleted the questionable data, others did not, and still otners stated that these effects would be averaged out over the length of the study.

The data analyst must also know if the samples were filtered before analysis. Past study data indicates that the inclusion of particulate "wash-out" material in bulk and wet-only samples as well as dry deposition in bulk samples changes the overall chemistry of the sample. Several studies routinely filtered the sample before analysis. This filtration of particulate matter, depending on technique and actual time when filtering occurred, could possibly change the resulting sample chemical composition and related analytical data. Whether glass or plastic collection devices were used could also affect the data. Galloway and Likens (1976) note the leaching of inorganic species into and out of glass collection devices and the loss of organic species with plastic devices. Other authors (Kadlecek and Mohnen, 1976; Norwegian Institute for Air Research, 1971) report similar findings. Metal ion losses in dilute samples have been repeatedly reported. To minimize this potential metal loss, various authors acidified a representative aliquot of the sample immediately following collection. Again, others did not. Sample storage techniques also vary among studies. Larger networks usually kept the sample in a cool, dark place. Some smaller networks either froze the sample or refrigerated the sample at 4°C. Galloway and Likens (1976) indicate that significant changes do not occur when samplers are stored at 4°C. Unfortunately, this storage technique is cost prohibitive for large national/international networks. How long a sample is stored before chemical analysis may also affect its integrity. A review of the literature reveals that the reported length of time from sample collection to sample analysis has varied by as much as 60 days. Some authors used chemical biocides to retard green algae growth in samples collected in warmer climates because the presence of algae changes the sample chemical composition. Obviously, the storage technique affects sample integrity at the time of chemical analysis.

Although procedures for collection of dry deposition are not as well documented, similar sampling variations are expected depending on technique (i.e., dust-fall buckets, ambient air monitors, or automated dry-only collection devices). Siting of the dry deposition collector is crucial; in particular, the height of the collector above ground level. Dry deposition samples 0 to 1 meter above ground level have been reported to be heavily influenced by contributions from the local terrain, as well as bird and vegetation contamination.

Data from special studies is also available for summation. Behrmann (1975), Pickerell et al. (1979), Anderson (1978), Cooper et al. (1976), and Gatz et al. (1971) report special one-of-a-kind samplers to monitor the change in the chemical composition of precipitation events at single sites. Special sampling procedures have been developed for the collection of snow (Galloway and Likens, 1976; Hagen et al., 1973), fog (Waller, 1963; Mrose, 1966), individual raindrops and canopy throughfall (McColl and Bush, 1978). Understanding these special sampling techniques is essential before these data are compiled or summarized.

The data analyst must also consider the various collection periods reported in past studies. Over the years, bulk samples have typically been collected on a monthly basis. However, wet deposition collection periods have ranged from event sampling to monthly sampling. Although clearly defined in terms of showers and thunderstorms, the definition of the beginning and ending of an event during a large frontal system varies from author to author. Monthly sampling is common in larger networks designed to monitor the trends in chemical composition over time. Daily or more frequent sampling is typically reported at individual sites with the objective to determine exact chemical loadings at specific sites. Weekly sampling is currently recommended by Galloway and Cowling (1978) as the minimum allowable sampling frequency to obtain usable wet deposition results. Dry deposition is commonly collected on a 1-to 2-month basis, as recommended by Galloway and Cowling (1978).

Each of the sampling and storage variations addressed above can affect the sample integrity and resulting data. In addition, site meteorology and collector efficiency also affect the sample. Summers and Whelpdale (1976) stress the existing need to document both scavenging and collection mechanisms involved with acid precipitation. Initial reviews of the most commonly used collectors have been conducted and are provided by Niemann (1979) and Galloway and Likens (1976). Additional comprehensive collector evaluations, including dry deposition collector efficiencies and species collected, along with a reevaluation of the meteorological mechanisms involved in acidic precipitation processes are needed. Before any past data summarization can be developed, a careful analysis of the sampling and storage procedures and collection mechanisms must be performed.

3.4.3 Analytical Techniques

3.4.3.1 Introduction--Analytical methodologies currently employed to analyze precipitation samples are, for the most part, state-of-the-art freshwater or natural water analytical techniques. Typical procedures are presented in Methods of Air Sampling and Analysis (Intersociety Committee, 1977a), Standard Methods for the Examination of Water and Waste Water (American Public Health Association, 1971) and U.S. Environmental Protection Agency's "Methods for Chemical Analysis of Water and Waste" (U.S. Envrionmental Protection Agency, 1979d). Theoretical detection limits and the quality of the data in terms of precision/accuracy for each technique are specified in the literature. Rainwater, however, is a dilute solution of chemical species, and represents extremely pure freshwater or natural water. Chemical analyses on rainwater yield results at or below the published analytical detection limits (Miller and Highsmith, 1976). Added precautions must be taken to minimize field/laboratory contamination (Likens, 1972), which is analytically indistinguishable from, and sometimes larger than, natural rainwater species contributions. To preclude changes in the chemical composition of the sample, analyses should occur within 24 hours after sample collection. Although operator and instrumentation dependent, laboratory analyses should meet or exceed the analytical precisions and accuracies presented in Table 3-6. Operator and instrumentation biases must be minimized through supporting internal and external quality assurance programs. Before 1975, no mechanism existed to externally evaluate the quality of the precipitation chemistry data being reported by the international precipitation laboratories. WMO instituted such an international quality assurance program in 1975. Potential errors in past data have subsequently been noted by Ridder (1978), Galloway et. al., (1979), Tyree et al. (1979), and Tyree (1981).

3.4.3.2 Analysis of Acidic Deposition Samples

3.4.3.2.1 Sample preparation. Wet deposition samples are allowed to equilibrate to room temperature before chemical analyses. Sample pH and conductivity are initially measured. Filtering or centrifuging of the sample may follow. A representative portion of the sample may then be acidified (HNO_3) to preserve the metal ion concentrations. Between analyses, samples are either stored in a dark, cool place or at 4°C. Dry deposition samples are dissolved with a known quantity of distilled water (typically 50 ml). Analytical procedures for these dissolved dry deposition samples are identical to the wet deposition analytical procedures described below.

3.4.3.2.2 Volume. Direct volume measurements, accuracy ± 3 percent, are made on the wet deposition sample with Class A graduated cylinders. Care must be taken to ensure that the sample is not contaminated by the labware used in this procedure. Indirect volume techniques include weighing the collection container before and after the sampling period or measuring the collection in a standard rain gauge (cylinder, tipping bucket, or weighing). Standard rain gauge accuracies are ± 0.02 in or better, depending on the manufacturer. The weighing rain gauge is

TABLE 3-6. RECOMMENDED PHYSICAL/CHEMICAL PARAMETERS FOR ANALYSIS

Parameter	Unit of report	Expected range	Suggested precision	Suggested accuracy
Volume (field)	inches	0.00-10.00	±.02"	±.02"
pH (field + lab)	pH	2.00-9.00	±.01pH	±.01pH
Conductivity (field + lab)	µS/cm	0.1-200.0	±5%	±5%
SO_4	mgS/l	0.1-10.0	±2%	±2%
NO_3	mgN/l	0.1-10.0	±2%	±2%
Cl	mgCl/l	0.1-10.0	±2%	±2%
NH_4	mgN/l	0.05-10.0	±3%	±2%
K	mgK/l	0.01-5.00	±2%	±2%
Ca	mgCa/l	0.01-5.00	±2%	±2%
Na	mgNa/l	0.01-10.00	±5%	±3%
Mg	mgMg/l	0.01-2.00	±2%	±2%
Acidity	µeq/l	1.0-500.0	±10%	±5%

preferred since it offers minimal evaporation loss and a higher degree of reliability over the tipping bucket rain gauge during intense storms.

3.4.3.2.3 pH. The pH is the measurement of the hydrogen ion activity (i.e., pH = -log $[H^+]$), commonly referred to as the free acid content of the solution. The pH of a typical United States wet deposition sample ranges between 4.0 and 5.0 pH units. Samples collected in more arid regions may range as high as pH 8.0, whereas samples collected in the Northeastern United States typically range from pH 3.5 to pH 4.5. Precipitation pH measurements were not reported prior to 1962. Instead, methyl orange indicator solution (endpoint pH = 4.4) (Skoag and West, 1965) was added to assess the sample acidity. Cogbill and Likens (1974) and Granat (1972) indirectly calculated and reported the pH's of precipitation samples taken prior to 1962. Currently, pH is electrometrically determined with a standard pH meter in conjunction with either glass/reference calomel electrodes or a combination electrode at 25°C. Three certified buffer solutions are used to calibrate the pH meter/electrode system in the pH range 3.50 to 7.50. Direct pH measurements are made on a representative portion of the sample. Measurements of pH are dependent on operator techniques and the condition of the electrode(s). Galloway et al. (1979); Ridder (1978); and Tyree et al. (1979) noted potential sources of errors in pH measurements. With proper care and quality equipment, pH results with a precision of ± 0.02 pH units and accuracy of ± 0.05 pH units should be obtainable (American Public Health Association, 1971).

3.4.3.2.4 Conductivity. The specific conductance of a wet deposition sample indicates the capability for that sample to carry an electrical current. Conductivity is related to the total concentration of dissolved ions, is directly determined on the sample with a standard Wheatstone bridge in conjunction with a calibrated conductivity cell at 25°C. Wet deposition sample conductivities normally range from ca. 10 to 200 μS/cm. Daily calibration of the conductivity meter and cell with freshly prepared standard KCl solution is required for accurate measurements. Operator techniques, the condition of the conductivity cell, and the quality of the standard KCl solutions determine the quality of data reported. Under careful supervision, conductivity measurements with precision and accuracy of 5 percent are obtainable (American Public Health Association, 1971).

3.4.3.2.5 Acidity. An acidity measurement indicates the capacity of the wet deposition sample to donate protons from both strong and weak acids. Numerous techniques have been reported to measure sample acidity. Each technique can yield a slightly different result (Tyree, 1981). Acidity values from -200 μeg/liter to +200 μeg/liter are routinely reported. The precision and accuracy of any acidity measurement dependents on the analytical technique employed and the ability of the operator to standardize and titrate minute quantities of highly diluted strong base. Tyree (1981) notes that the operator is the key to good acidity measurements. Both the presence of substances such as carbon dioxide, aluminum, iron, and ammonium, and the method endpoint pH influence the results.

3.4.3.2.5.1 pH. See Section 3.4.3.2.3. Depending on the actual sample pH, acidity based on a pH measurement yields either the strong acid proton component (sample pH <4.5) or the strong acid component plus some undetermined contribution from the weak acid component (sample pH >4.5). Acidity based on pH alone is not considered conclusive.

3.4.3.2.5.2 Titrimetric. Various titrimetric endpoint procedures are available.

Phenolphthalein Endpoint. The rainwater sample is titrated with standardized 0.01 to 0.001 N strong base (NaOH) to the phenolphthalein endpoint (8.0 to 9.6 pH units per Skoag and West, 1965). Precision and accuracy (± 5 percent) depend on the ability of the operator to standardize and deliver minute quantities of dilute base and the repeatability of the endpoint color (American Public Health Association, 1971).

WMO. A prescribed quantity of strong acid (H_2SO_4) is added to the sample, lowering the sample pH to less than 4.0 and thus removing the CO_2. The sample is titrated against standardized base until the sample pH, monitored via a pH meter, reads pH 5.6. Precision (± 0.02 pH units) and accuracy (± 0.05 pH units) are dependent on the quality of the pH meter and standardized base, the condition of the electrodes, and operator technique.

American Public Health Association. Strong acid is added to lower the sample pH below 4.0. Hydrogen peroxide is then added. The sample is boiled to eliminate CO_2, cooled to room temperature and titrated electrometrically with strong base to pH 8.3 (EPA method endpoint =

8.2). The U.S. Environmental Protection Agency (1979) reports a standard deviation of 1 to 2 mg $CaCO_3$/liter and bias of ca. ± 20 percent for sample measurements in the 10 to 120 mg $CaCO_3$/liter range.

Likens (1972). Nitrogen is bubbled through the sample to eliminate any CO_2 interference. Samples are titrated to pH 9.00 with standard base. The accuracy of the pH meter is reported to be ± 0.03 pH units (1972). Following this technique, Hendry and Brezonik (1980) titrated samples to pH 7.00 endpoint.

Coulometric/Potentiometric. The sample is titrated with cathodically generated hydroxyl ion (OH^-) [i.e., (-) reference electrode/test solution/glass electrode (+)] as outlined by Liberti et al. (1972) and Askne et al. (1973). Gran plots (Gran, 1952) are interpreted to determine the strong and weak acid contributions. Liberti et al. (1972) report a ± 5 percent standard derivation and 0.1 mg/liter H_2SO_4 sensitivity when analyzing strong acids. The Norwegian Institute for Air Research (NAIR) (1971) reported a 2 to 5 µeq acidity/liter standard deviation in rainwater samples having 10^{-4}-10^{-5} acidity concentrations. Askne et al. (1973) observed "exact agreement" in strong acid analyses, but only "reasonable-to-good agreement" with samples containing various concentrations of strong and weak acids. Tyree et al. (1979) and Krupa et al. (1976) also observed difficulties in determining strong/weak acid contributions in rainwater samples using this technique.

3.4.3.2.5.3 Ion Balance. Granat (1972) and Cogbill and Likens (1974) reported a technique to calculate sample pH's based on the total ionic strength. In this technique, the charge difference in favor of the anion concentration is related to the sample hydronium ion concentration. Possession of accurate analytical data for the individual principal ions is essential. The overall precision and accuracy of this technique is no better than the summation of precisions and accuracies of the analytical methods used to determine the individual ionic species. Tyree et al. (1979) states that this technique could possibly be used to determine the strong acid contribution in samples with observed pH 5.6 or below.

3.4.3.2.6 Sulfate ($SO_4^=$). Analytical procedure for sulfate analysis are described in Section 3.3.4.1.1. Typical wet deposition samples contain 0.1 to 5.0 mg $SO_4^=$/liter.

3.4.3.2.7 Ammonium (NH_4^+). Ammonium concentration of 0.1 to 1.0 mg N/liter are normally observed in wet deposition samples. Two techniques (ion selective electrode and indophenol colorimetry) are discussed in Section 3.3.4.2. Manual Nesslerization techniques (American Public Health Association, 1971) are commonly used. The Nessler reagent is thoroughly mixed with the sample (ca. 30 minutes). The characteristic yellow color is photometrically determined (425 mµ with 1 cm cell path). Analyses of samples containing 0.2 mg N/liter typically produce results with ± 0.12 mg N/liter standard deviation and ± 18 percent bias (U.S. Environmental Protection Agency, 1979).

3.4.3.2.8 Nitrate (NO_3^-). The rainwater sample's nitrate (normal concentration range 0.1 to 5.0 mg N/liter) is quantitatively reduced to nitrite by the addition of hydrazine sulfate

(Kamphake et al., 1967) or by passing the sample through a copper-cadmium column (U.S. Environmental Protection Agency, 1979d). The addition of sulfanilamide and N-(1-napthyl)-ethylene diamine dihydrochloride yields a highly colored azo dye measureable colorimetrically at 520 nm. Automated techniques (U.S. Environmental Protection Agency, 1979c) minimize operator error and increase the sample throughput. A second analysis without the nitrate reduction step is required to correct for sample nitrite concentration. Precision and accuracy of ± 5 percent are expected with samples above 1 mg N per liter. Butler et al. (1978) and Tyree et al. (1979) report comparable sensitivity, precision, and accuracy using an automated IC technique (see Section 3.3.4.2.2.4).

3.4.3.2.9 Chloride (Cl^-). Various manual and automated procedures are used to determine chloride in rainwater in the concentration range 0.1 to 10.0 mg Cl^-/liter with precision ca. ± 0.2 mg Cl/liter. The WMO method adds mercuric nitrate and diphenylcarbazone-bromophenol blue to the sample forming mercuric chloride. The excess mercury complexes with the indicator to form a blue-violet dye measured photometrically at 525 nm. Zall et al. (1956) displace the thiocyanate ion (SCN^-) in $Hg(SCN)_2$ and form $HgCl_2$. In the presence of excess iron, the highly colored dye $[Fe\ (SCN)^{+}_{+}]$ is formed and can be photometrically measured at 460 μm. The automated ferricyanide procedure (U.S. Environmental Protection Agency, 1979d) is preferred over the manual methods since operator/standard solution errors are minimized. Automated IC techniques (Butler et al., 1978; Tyree et al., 1979 and Section 3.3.4.1.1.4) yield comparable results.

3.4.3.2.10 Fluoride (F^-). Fluoride in wet deposition (range 0.01 to 0.1 mg F/liter) is generally determined by the ion selective electrode technique. The condition of the fluoride ion selective electrode is critical. Analysis of synthetic samples containing 0.85 mg F/liter yielded results with a 3.6 percent relative standard deviation and 0.7 percent relative error (American Public Health Association, 1971). Automated IC techniques (Butler et al., 1978; Tyree et al., 1979; and Section 3.3.4.1.1.4) yield similar results.

3.4.3.2.11 Trace Metals. Techniques used to determine trace metal concentration in rainwater are described in Section 3.3.4.3. Observed metal concentration ranges generally approximate the lower detection limit for flame atomic absorption metal analysis.

3.4.4 Interlaboratory Comparisons

WMO (1975) instituted an international interlaboratory program to describe the quality of the wet deposition chemistry data being reported by the various WMO laboratories. Participation in this program is voluntary. The results of three comparisons on synthetic rainwater samples (WMO, 1976; Thompson, 1978; WMO, 1980) have been reported previously. The United States Department of Energy (DOE) sponsored a similar round robin (Battelle Pacific Northwest Laboratories, 1979) on both simulated and composited rainwater samples. Tyree et al. (1979) and Tyree (1981) discuss the WMO and DOE results.

Three physical analyses (pH, conductivity, and acidity) are most frequently reported and compared. Conductivity and pH data have been extracted from the three WMO reports and are

TABLE 3-7. RESULTS OF WMO INTERCOMPARISONS ON SYNTHETIC PRECIPITATION SAMPLES

	pH (pH Units)							Conductivity (μS/cm)							Acidity (μeq/l)					
Session	Sample type	$\bar{x}^b$	$\sigma_x{}^c$	N^d	High x	Low x	Session	Sample type	$\bar{x}$	σ_x	N	High x	Low x	Session	Sample type	$\bar{x}$	σ_x	N	High x	Low x
1976	A	5.45	.74	17	6.40	3.65	1976	A	6.9	4.3	17	22.0	3.9	1976	NOT REPORTED BY WMO					
	B	5.53	.76	18	7.22	3.85		B	17.3	4.9	18	28.0	20.0							
	C	5.53	.52	17	6.20	4.10		C	56.3	4.8	17	62.0	44.0							
	D	5.56	.41	18	6.10	4.20		D	109.3	8.1	18	119.0	84.0							
1978	A	5.66	.49	25	6.54	4.61	1978	A	6.7	3.0	25	19.0	3.9	1978	NOT REPORTED BY WMO					
	B	5.77	.51	25	7.07	4.65		B	17.9	8.8	25	57.0	9.0							
	C	5.60	.44	25	6.58	4.54		C	52.4	12.0	25	67.5	19.1							
	D	5.65	.39	25	6.64	4.79		D	103.6	23.9	25	132.0	37.9							
1980	71	4.21	.16	26	4.55	3.80	1980	71	29.1	4.0	25	37.3	18.3	1980	71	70.0	36.7	22	206.0	18.9
	72	4.02	.11	26	4.17	3.72		72	80.4	9.1	25	95.6	57.3		72	106.3	43.6	22	260.0	29.2
	73	5.58	.19	26	6.02	5.17		73	195.9	21.6	25	224.0	132.0		73	25.3	63.7	18	202.0	-37.0
	[a]74	3.91	.16	24	4.30	3.60		[a]74	64.4	8.0	23	81.5	48.0		[a]74	10.9	16.1	22	68.0	4.7

[a] Sample contains only H_2SO_4

[b] $\bar{x}$ = sample mean = $\frac{\Sigma x_i}{i}$

[c] σ_x = standard deviation =

$$\sqrt{\frac{\Sigma(x_i-\bar{x})^2}{N-1}}$$

[d] N = number of laboratories.

provided in Table 3-7. WMO did not summarize the acidity measurement results in the first and second analysis sessions. The synthetic samples used in the first two sessions contained only weak acids. The laboratory results indicated that the WMO laboratories, as a whole, could not perform acidity measurements on samples containing only weak acids. Four new samples were used in the third WMO analysis session. Three of the third analysis session samples (samples 71, 72, 73) contained both weak and strong acids. Sample type 74 contained only strong sulfuric acid. The results of the acidity measurements reported in the third analysis session have also been extracted. Table 3-8 lists the among laboratories percent coefficient of variation (% cv) by session for those chemical analyses routinely performed by the WMO participants, where

$$\%\ cv = \frac{\sqrt{\frac{\Sigma(d_i-\bar{d})^2}{N-1}}}{\bar{x}} \times 100\% \qquad (3\text{-}3)$$

Improvement in the analysis for a given constituent by the WMO laboratories, as a whole, is indicated by decreasing percent cv. from session 1 to session 3. In general, the WMO laboratories showed improvement from session 1 to session 3.

WMO and DOE intercomparison results highlight the difficulties encountered in analyzing dilute precipitation samples. When comparing data from various studies, the data analyst must include the appropriate biases resulting from the laboratory's sampling and storage techniques as well as the ability of the laboratory to perform chemical analyses on the sample.

TABLE 3-8. COEFFICIENTS OF VARIATION OF WMO INTERCOMPARISONS ON SYNTHETIC PRECIPITATION SAMPLES

	Among laboratories percent coefficient of variation (% cv.)		
	% cv by session		
Constituent	1976	1978	1980
pH	10	8	3.4
Conductivity	15	22	12
SO_4	13	24	34
NH_4	38	32	33
NO_3	79	64	74
Cl	58	24	25
Ca	27	25	25
K	32	30	22
Ma	21	8	99
Na	29	27	19

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APPENDIX 3A

FILTER: Gelman Type A, glass fiber

ΔP, cm Hg	1	1.5	3	10
V, cm/sec	11.2	16.9	32.7	108
D_p, μm	PENETRATION			
0.035	<0.0001	<0.0001	<0.0001	0.0008
0.10	<0.0001	<0.0001	<0.0001	0.00054
0.30	<0.0001	<0.0001	<0.0001	<0.00007
1.0	<0.0001	<0.0001	<0.0001	<0.0002

FILTER: Ghia S2 37PJ 02, teflon membrane, 2.0 μm pore

ΔP, cm Hg	1	3	10
V, cm/sec	23.4	64.1	187
D_p, μm	PENETRATION		
0.035	<0.0002	0.0011	0.0005
0.10	<0.00006	0.00008	<0.00024
0.30	<0.00007	<0.00007	<0.00022
1.0	<0.00007	<0.00009	<0.00008

FILTER: Whatman No. 1, cellulose fiber

ΔP, cm Hg	1	3	10	30
V, cm/sec	6.1	17.4	47.6	102
D_p, μm	PENETRATION			
0.035	0.56	0.52	0.34	0.058
0.10	0.46	0.43	0.13	0.0071
0.30	0.16	0.044	0.0049	0.00051
1.0	0.019	0.034	0.0044	0.00042

Table A-1. Fractional penetration by particle size and face velocity for three selected filter types (Liu et al., 1978a).

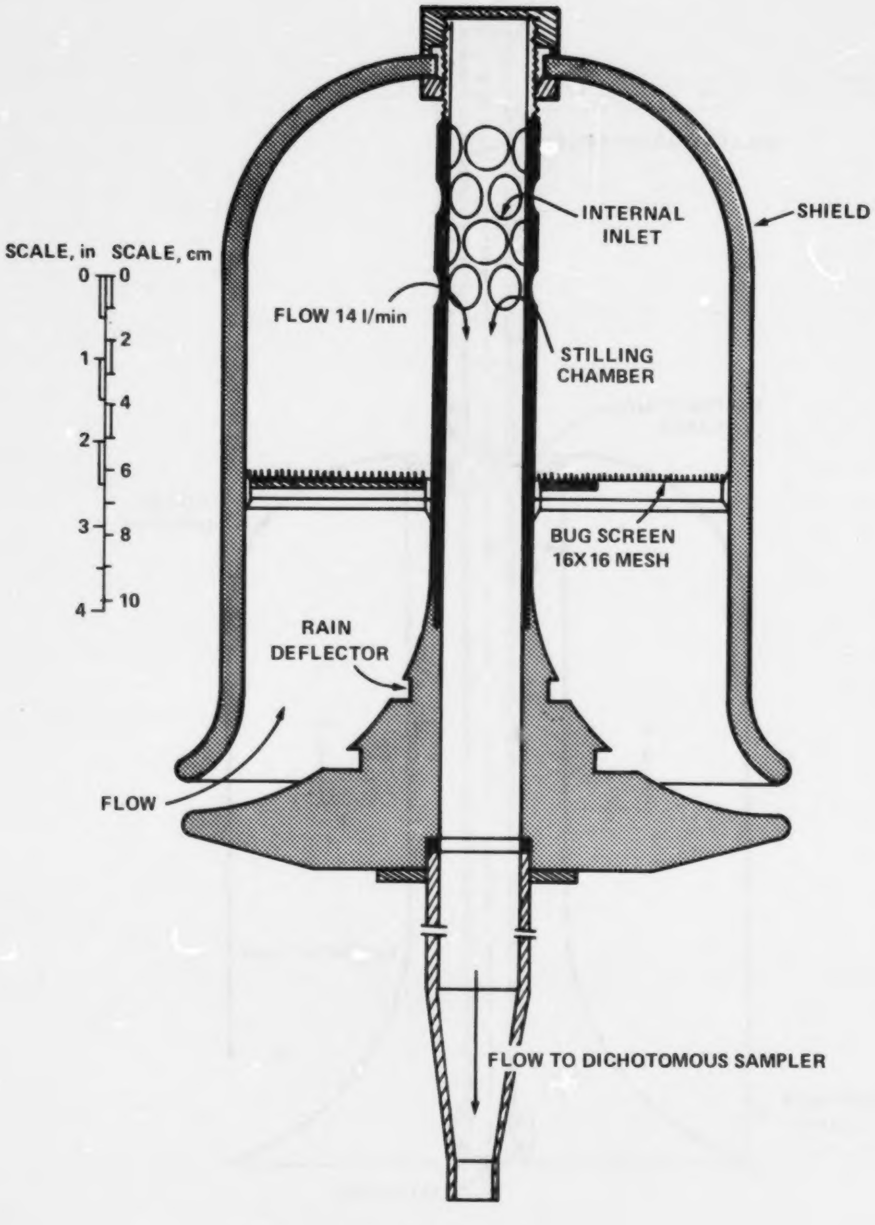

INTERNAL INLET
SHIELD
SCALE, in
SCALE, cm
0
0
2
1
4
2
6
3
8
4
10
FLOW 14 l/min
STILLING CHAMBER
BUG SCREEN 16X16 MESH
RAIN DEFLECTOR
FLOW
FLOW TO DICHOTOMOUS SAMPLER

Figure 3A-1. Early inlet for the dichotomous sampler.

Source: Stevens and Dzubay (1978).

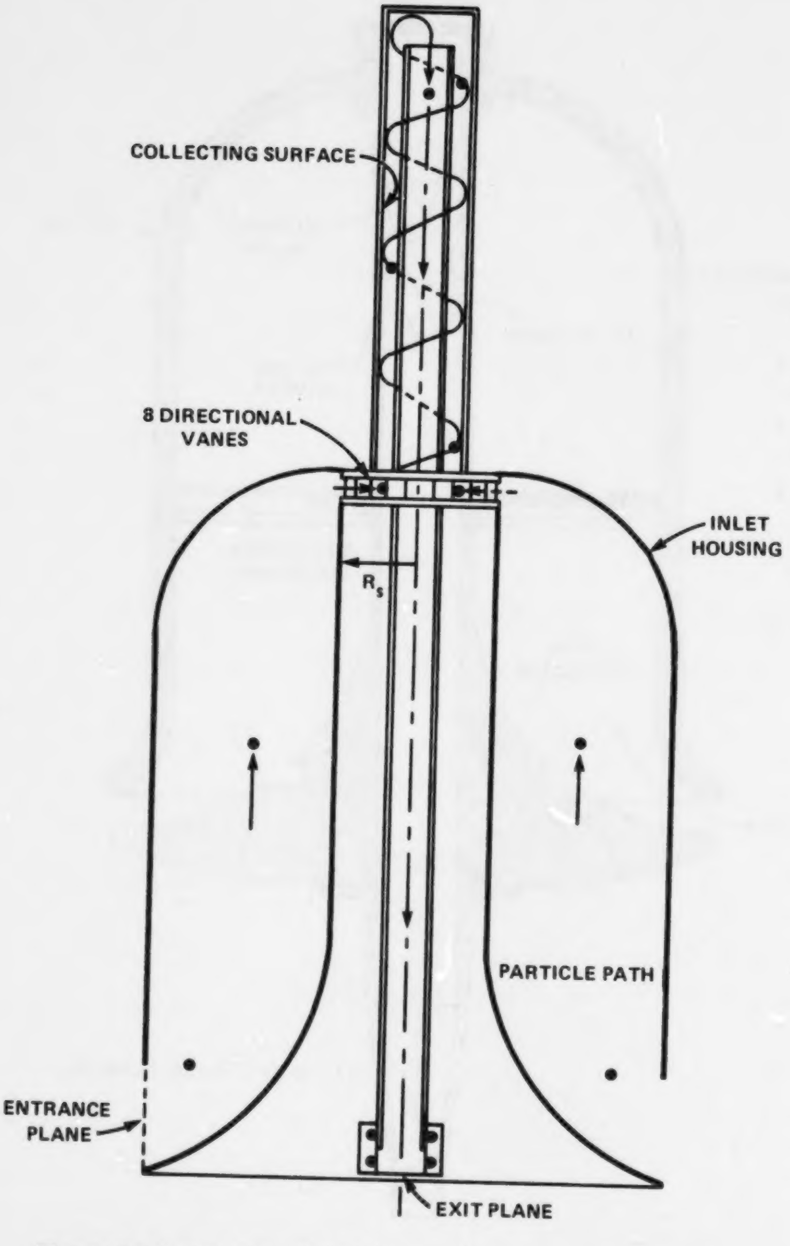

COLLECTING SURFACE
8 DIRECTIONAL VANES
INLET HOUSING
R_s
PARTICLE PATH
ENTRANCE PLANE
EXIT PLANE

Figure 3A-2. Wedding IPM inlet, section view, not to scale. Source: Wedding (1980).

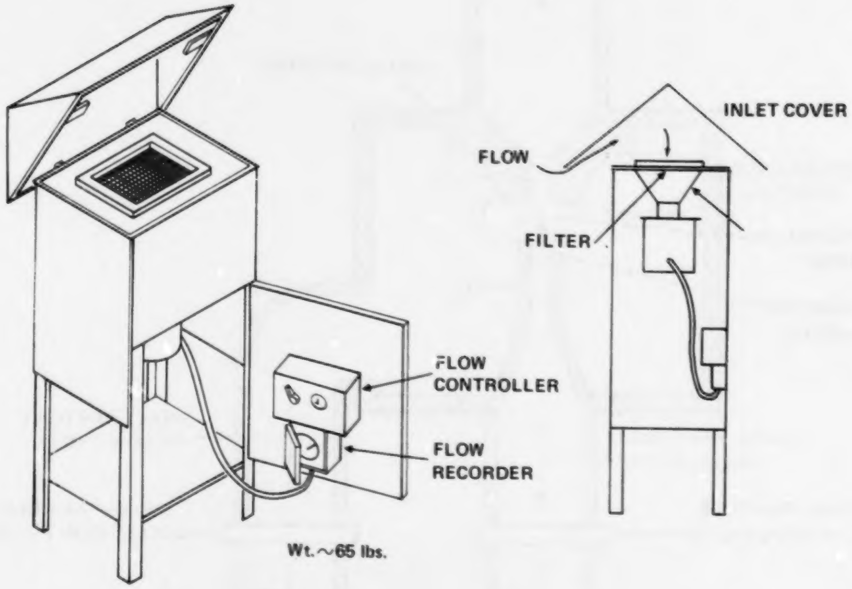

FLOW
CONTROLLER
FLOW
RECORDER
Wt. ~65 lbs.
INLET COVER
FLOW
FILTER

Figure 3A-3. TSP Hi-Vol.

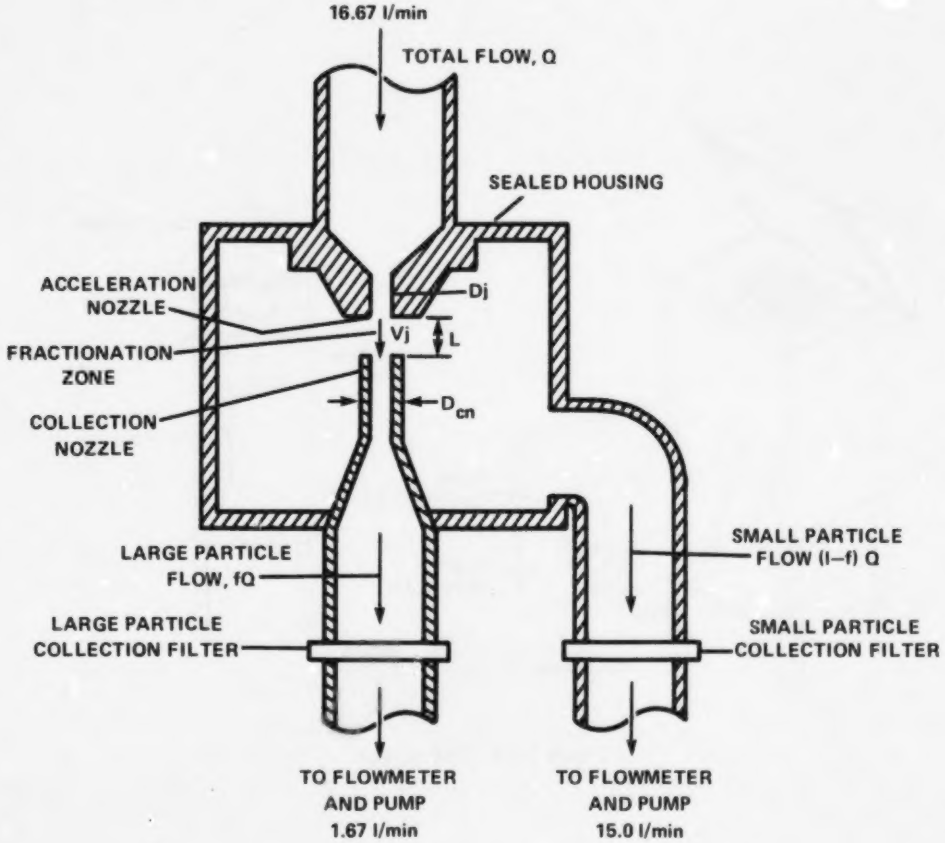

16.67 l/min
TOTAL FLOW, Q
SEALED HOUSING
ACCELERATION NOZZLE
Dj
Vj
L
FRACTIONATION ZONE
COLLECTION NOZZLE
D_{cn}
LARGE PARTICLE FLOW, fQ
SMALL PARTICLE FLOW (I–f) Q
LARGE PARTICLE COLLECTION FILTER
SMALL PARTICLE COLLECTION FILTER
TO FLOWMETER AND PUMP 1.67 l/min
TO FLOWMETER AND PUMP 15.0 l/min

Figure 3A-4. Dichotomous sampler separator.

Source: Loo et al. (1979)

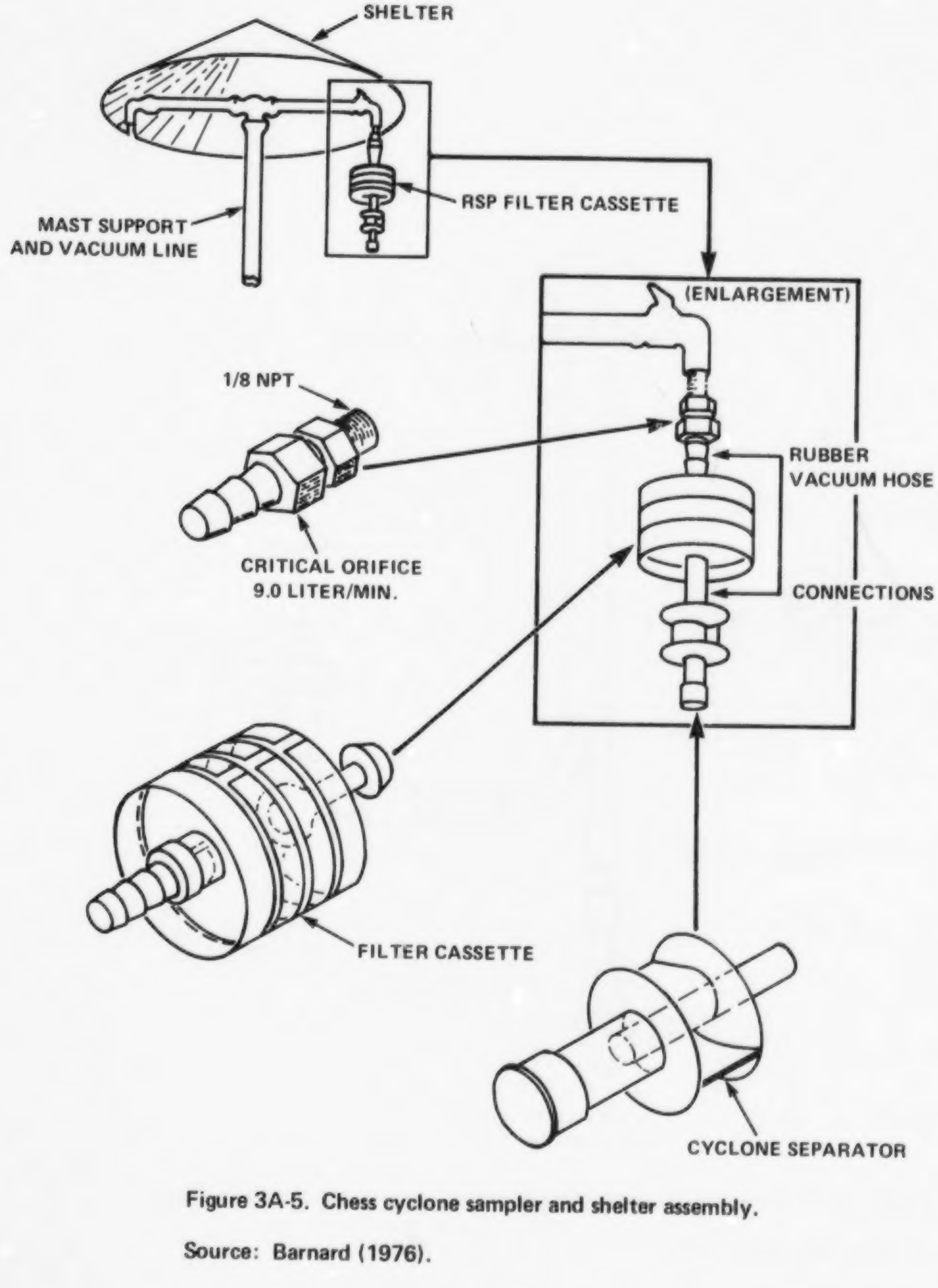

SHELTER
MAST SUPPORT AND VACUUM LINE
RSP FILTER CASSETTE
(ENLARGEMENT)
1/8 NPT
RUBBER VACUUM HOSE
CRITICAL ORIFICE 9.0 LITER/MIN.
CONNECTIONS
FILTER CASSETTE
CYCLONE SEPARATOR

Figure 3A-5. Chess cyclone sampler and shelter assembly.

Source: Barnard (1976).

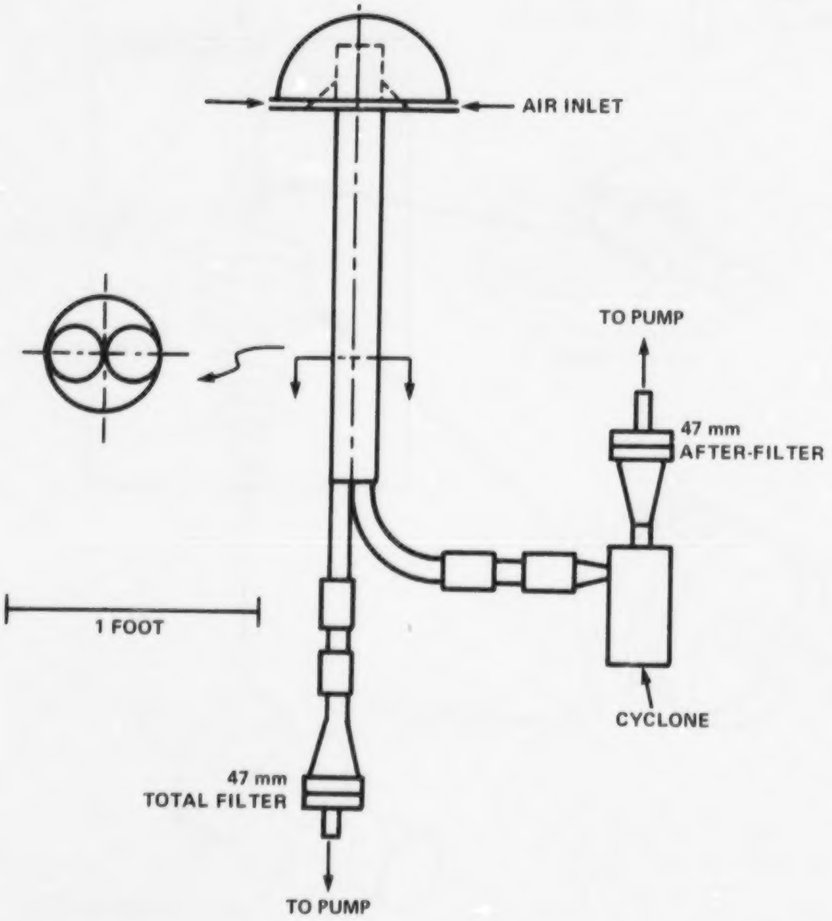

AIR INLET
TO PUMP
47 mm
AFTER-FILTER
1 FOOT
CYCLONE
47 mm
TOTAL FILTER
TO PUMP

Figure 3A-6. Assembly for sampling with a total filter and cyclone in parallel.

Source: John et al. (1978)

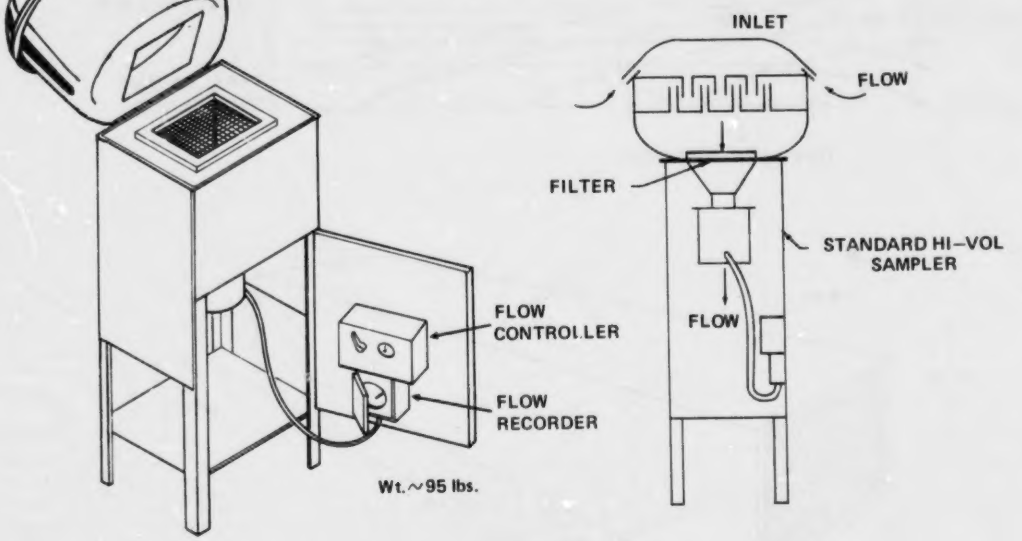
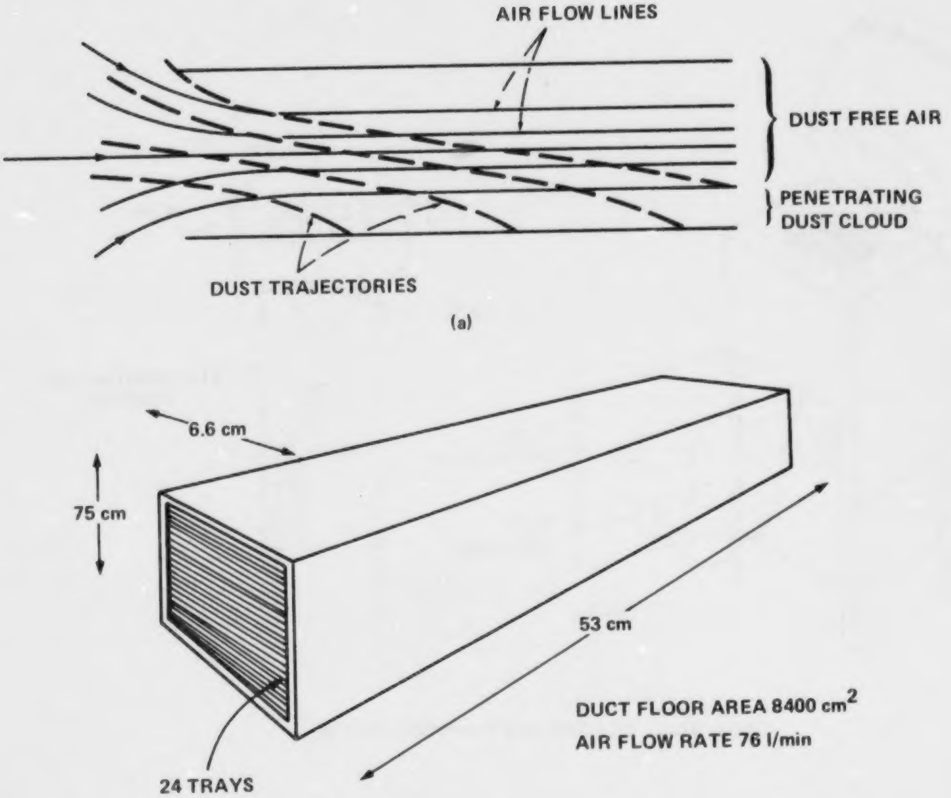

FLOW CONTROLLER
FLOW RECORDER
Wt. ~95 lbs.
INLET
FLOW
FILTER
STANDARD HI–VOL SAMPLER
FLOW

Figure 3A-7. Size-Selective Inlet (SSI) Hi-Vol.


AIR FLOW LINES
DUST FREE AIR
PENETRATING DUST CLOUD
DUST TRAJECTORIES
6.6 cm
75 cm
53 cm
DUCT FLOOR AREA 8400 cm²
AIR FLOW RATE 76 l/min
24 TRAYS

(a)

(b)

Figure 3A-8. The horizontal elutriator designed to match the BMRC deposition curve.

Source: Hamilton and Walton (1961).

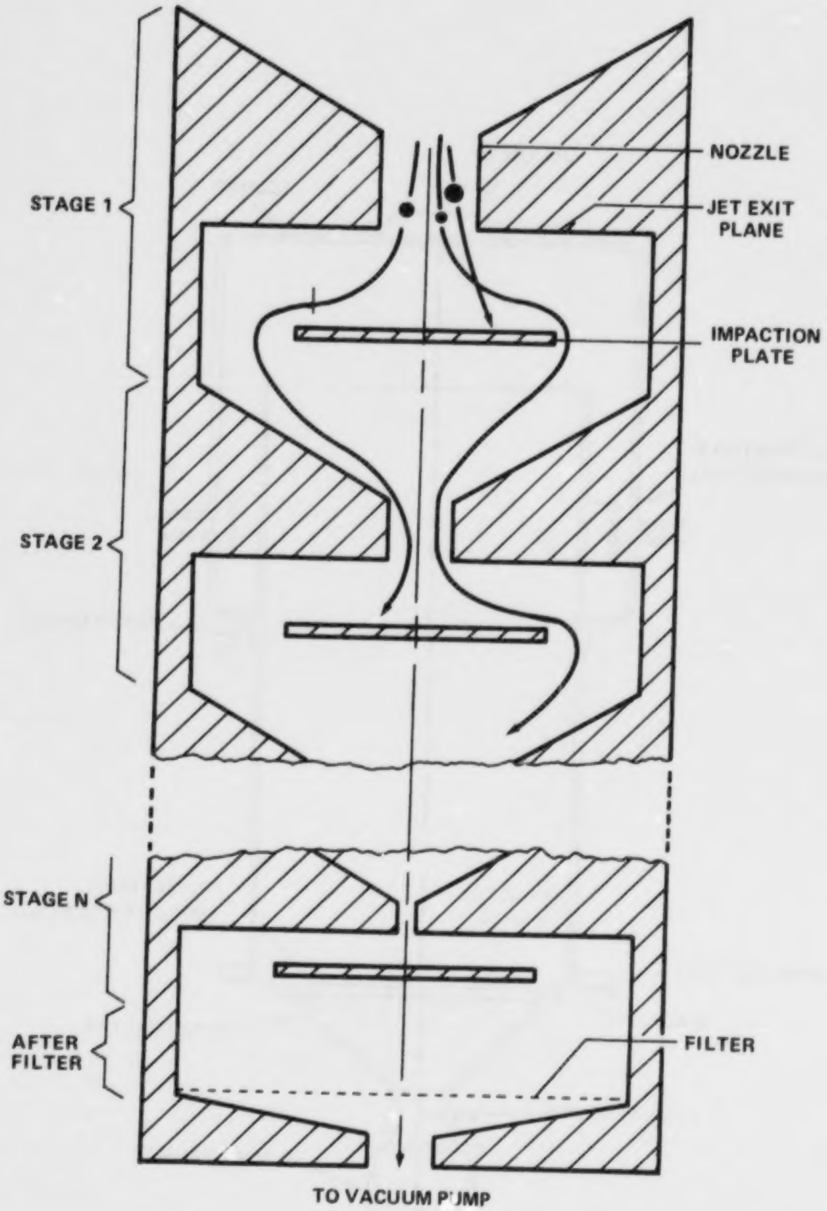

NOZZLE
STAGE 1
JET EXIT PLANE
IMPACTION PLATE
STAGE 2
STAGE N
AFTER FILTER
FILTER
TO VACUUM PUMP

Figure 3A-9. Schematic diagram of a cascade impactor.

Source: Marple and Willeke (1979).

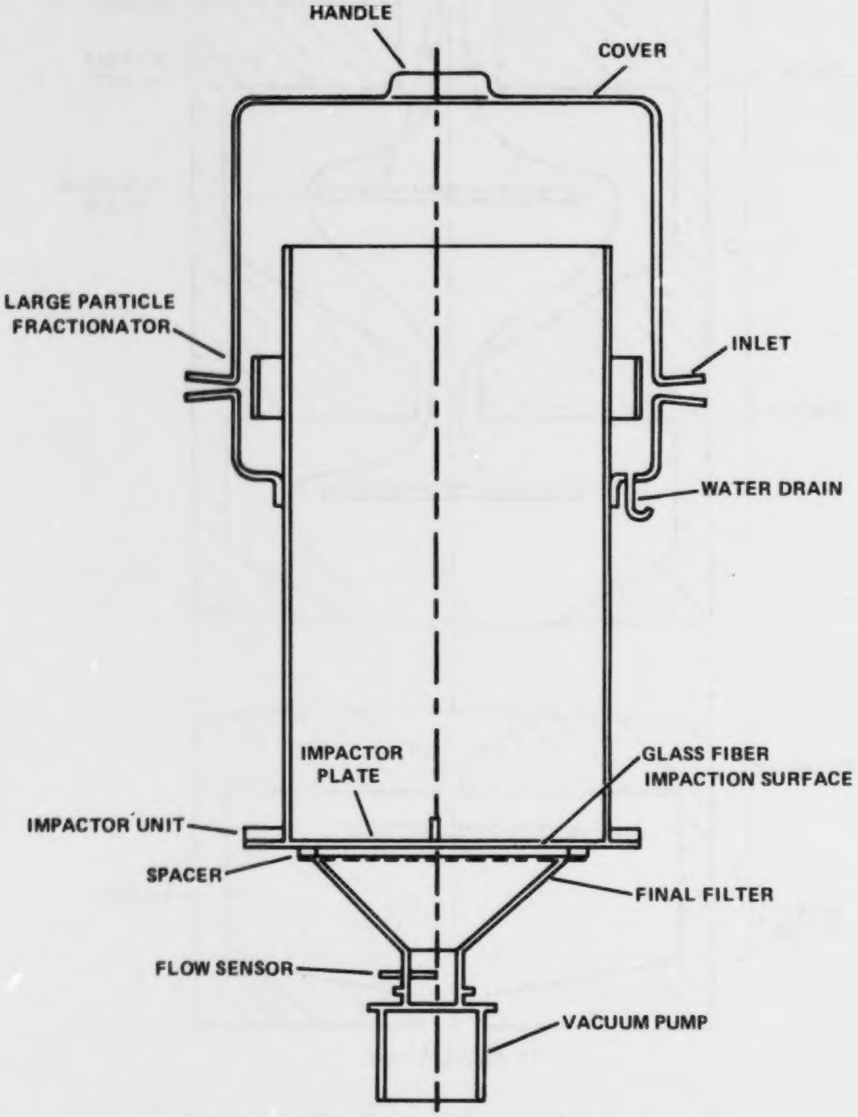
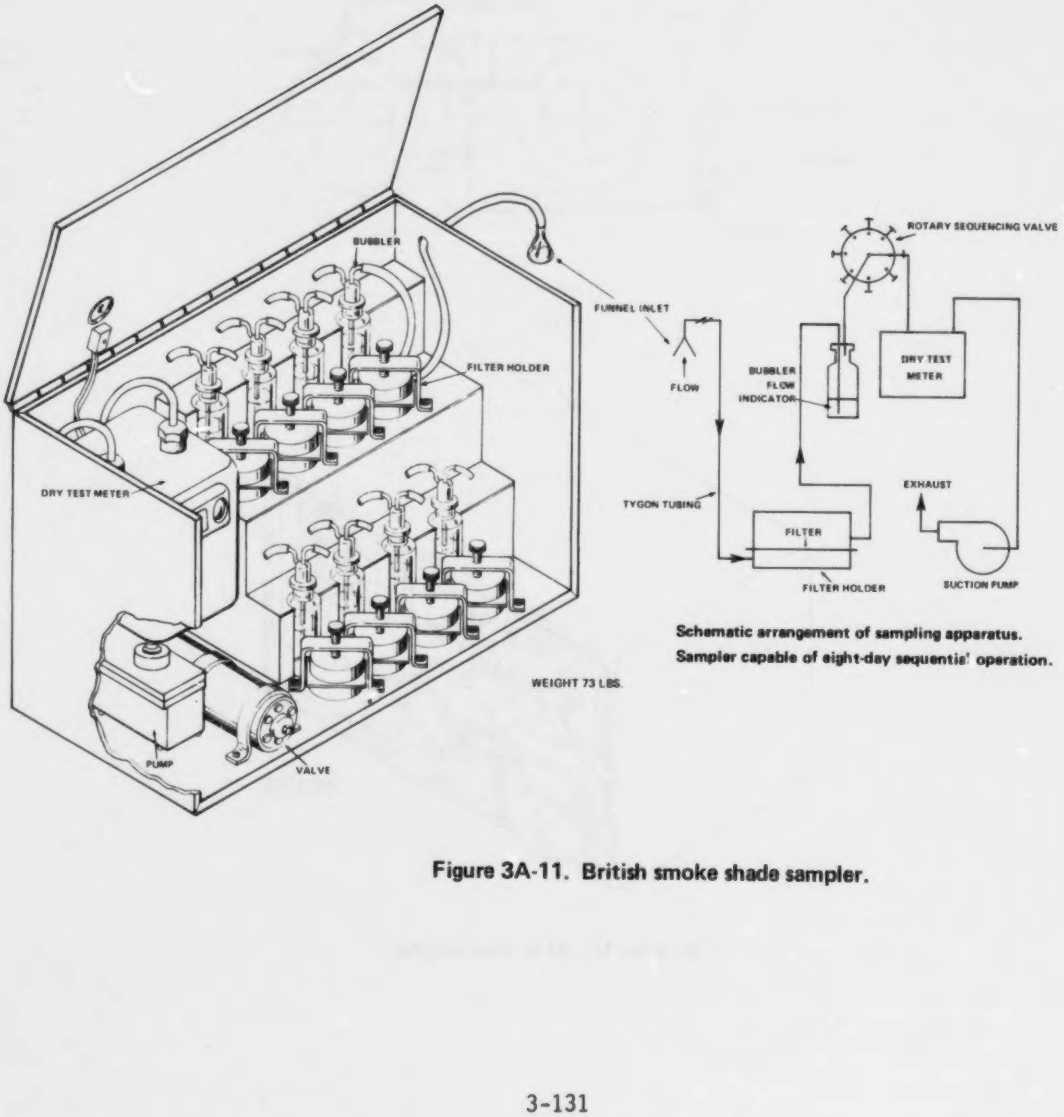

HANDLE
COVER
LARGE PARTICLE FRACTIONATOR
INLET
WATER DRAIN
IMPACTOR PLATE
GLASS FIBER IMPACTION SURFACE
IMPACTOR UNIT
SPACER
FINAL FILTER
FLOW SENSOR
VACUUM PUMP

Figure 3A-10. Cross section schematic of the CHAMP aerosol sampler.

Source: Ranade and Osdell (1978).


BUBBLER
FILTER HOLDER
DRY TEST METER
WEIGHT 73 LBS.
PUMP
VALVE
FUNNEL INLET
FLOW
TYGON TUBING
FILTER
FILTER HOLDER
BUBBLER FLOW INDICATOR
ROTARY SEQUENCING VALVE
DRY TEST METER
EXHAUST
SUCTION PUMP

Schematic arrangement of sampling apparatus.
Sampler capable of eight-day sequential operation.

Figure 3A-11. British smoke shade sampler.

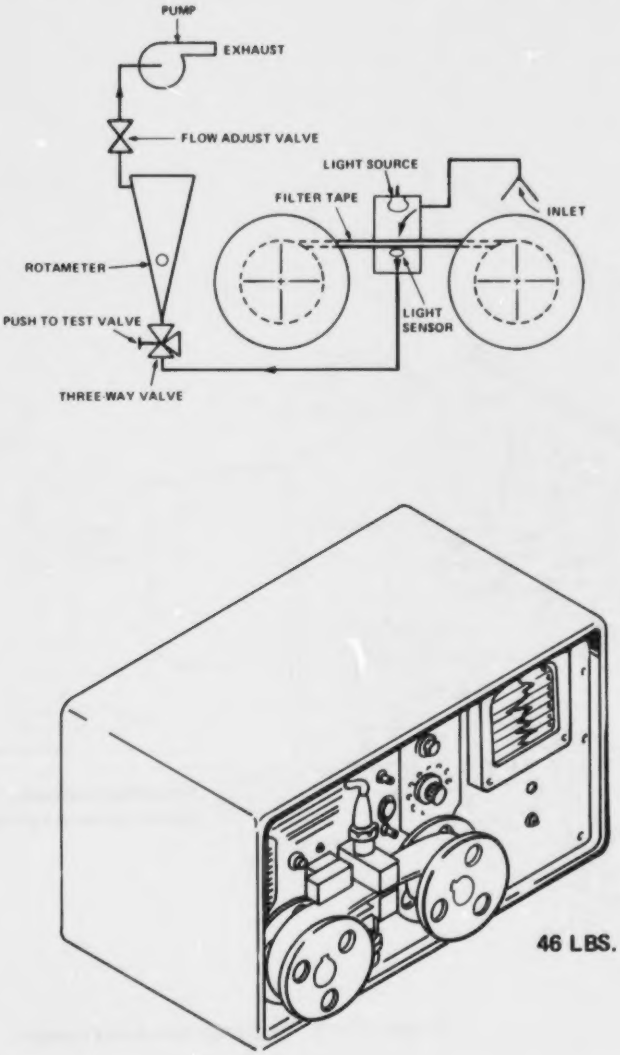
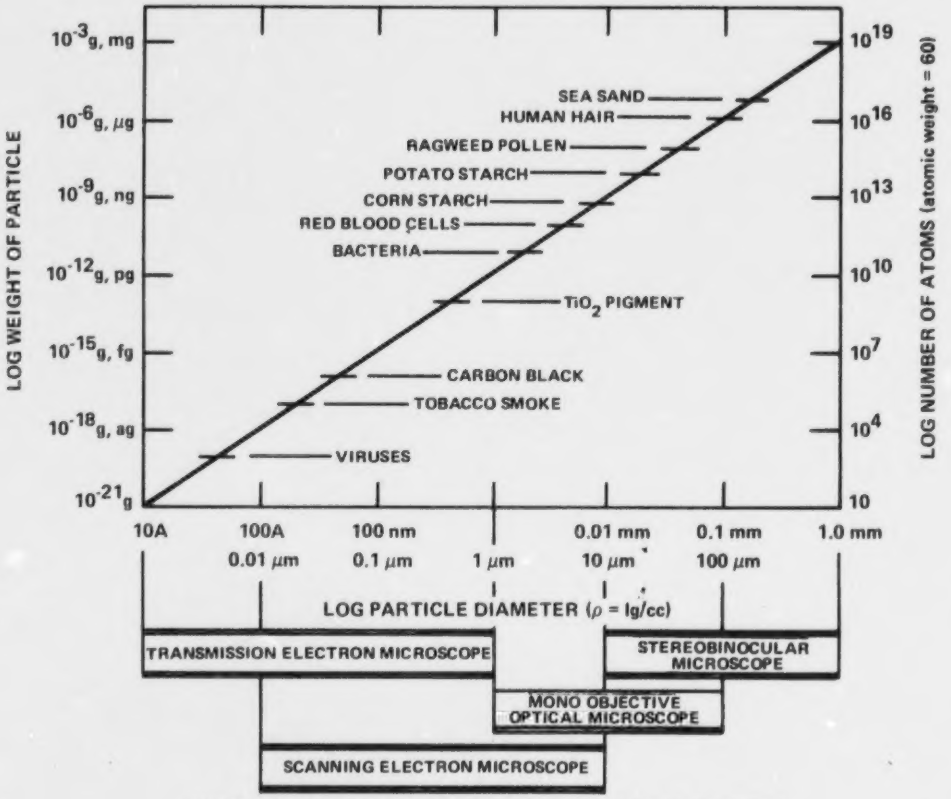

PUMP
EXHAUST
FLOW ADJUST VALVE
LIGHT SOURCE
FILTER TAPE
INLET
ROTAMETER
PUSH TO TEST VALVE
LIGHT SENSOR
THREE-WAY VALVE
46 LBS.

Figure 3A-12. AISI tape sampler.



CHOICE OF MICROSCOPE FOR PARTICLE SIZE MEASUREMENT

Figure 3A-13. Relationship between particle size, diameter and number of atoms for the light and electron microscope range.

Source: McCrone and Delly (1973).

4. SOURCES AND EMISSIONS

4.1 INTRODUCTION

This chapter highlights the magnitude and characteristics of natural and anthropogenic sources and emissions of particulate matter and sulfur oxides. Natural emissions are defined as those not caused by human activities, such as volcanoes and the biosphere. Manmade sources include stationary point sources (e.g., utility power plants, industrial facilities, etc.), fugitive industrial and non-industrial sources (e.g., roadway dust), and transportation sources (e.g., vehicle exhausts). Each of these emissions categories is discussed further in this chapter.

Chapters 4, 5, and 6 present the information concerning the relationship between emissions and ambient air concentrations. The information in Chapter 4 concerning the sources and emissions of particulate matter and sulfur oxides relates directly to the chapters in this document which discuss pollutant effects on visibility, acidic deposition, and health. Chapter 5 summarizes measured ambient pollutant concentrations and characteristics. Chapter 6 presents what is known about the complex processes that alter and disperse the emitted substances as they move through the atmosphere.

The issue of the relationship between emission intensity and possible effects on humans is important, but the proximity of emissions to humans can often be more important than relative intensity. For example, mass emissions from residential fuel combustion (home heating) and transportation sources are minor on a national level. Since they are emitted in highly populated areas and close to ground level, however, they are more likely to affect human health and welfare. On the other hand, dust from unpaved roads appears significant in many areas, but unpaved roads are more prevalent in rural areas, and their influence tends to be highly localized. Conversely, although some natural source emissions can be fairly intense (volcanic ash or sulfur from marshlands, for example), their effects are lessened, in gereral, because they tend to be distributed fairly broadly nationwide. Consequently, simple comparisons of total national tonnages of manmade vs natural emissions will seldom reflect the impact that localized manmade sources can have on an area's air quality. For these reasons, certain manmade emission sources, particularly stationary point sources, have been given a greater share of the attention in this chapter.

A number of other issues are discussed here briefly or not at all. Predictions of future emissions trends have not been presented because of the complexities of supporting assumptions. Documents in which adequate discussions of assumptions can be found are referenced. In many cases, data on the particle size distribution and chemical composition of particulate emissions are incomplete or inadequate. Available data have been briefly summarized. Also, discussion of the effects of control devices on emission particle size distributions has been limited. Documents that discuss these effects thoroughly are referenced.

4.2 DATA SOURCES AND ACCURACY

The most important information presented in this chapter concerns emission quantities and characteristics. Though this information was gathered from the best and most recent literature available, problems are still apparent. Specifically, estimates of emission quantities vary, as do those of emission characteristics.

Emission quantities are typically estimated using emission factors. (The impossible alternative would be direct measurement of pollutants from each emission point.) Emission factors relate the quantity of pollutants emitted to an indicator of activity such as production capacity or quantity of fuel burned. Because emission factors are statistical averages, they do not precisely reflect emissions from individual sources. When a large number of sources are considered, however, a reasonable estimate of total emissions can be obtained. Therefore, the percentage error associated with emission estimates decreases as the geographic area studied increases (from the local to the regional to the national scale).

Table 4-1 illustrates the variability of specific emission estimates that can be associated with the use of different estimation approaches. In the table, "estimates" refers to National Air Pollutant Emission Estimates, 1970-1978 (U.S. Environmental Protection Agency, 1980a). Emissions totals in that document were obtained from one calculation performed at the national level by use of total national activity levels and national average emission factors for each source category. "NEDS" (National Emissions Data System) refers to the 1977 National Emissions Report (U.S. Environmental Protection Agency, 1980b). NEDS national emissions totals were obtained by adding the emissions from individual facilities and may be affected by mistakes, biases, and omissions. Therefore, the "Estimates" are judged by the U.S. Environmental Protection Agency to be the most reliable national estimates presently available. The NEDS State emissions totals, presented in Section 4.5.2 are the best available at the State level. However, neither of these totals should be regarded as precise, for the reasons given above. Nevertheless, such emission estimates do provide useful indications of the relative contributions from various source categories.

TABLE 4-1. TWO EPA ESTIMATES OF 1977 EMISSIONS OF PARTICULATE MATTER AND SULFUR OXIDES (10^6 METRIC TONS PER YEAR)

Source Category	Particulate Matter		Sulfur Oxides	
	Estimates	NEDS	Estimates	NEDS
Fuel combustion	4.8	3.6	22.2	22.7
Industrial processes	6.4	3.9	4.2	5.1
Solid waste disposal	0.5	0.4	0.0	0.0

Attempts to obtain more than rough estimates of fugitive industrial and nonindustrial particulate emissions also present problems. Industrial process fugitive particulate emissions, or process fugitives, include most industrial particulate emissions not passing through a stack or another identifiable emission point. Process fugitive emissions are difficult to estimate because of the lack of engineering data and adequate information on emission factors. In one reference (Zoller et al., 1978) these emissions were estimated at 3.4 x 10^6 metric tons per year. However, the U.S. Environmental Protection Agency's "Estimates" include "rough estimates of fugitive particulate emissions from industrial processes." Therefore, the particulate emission estimates alluded to under the industrial processes category discussed in this chapter probably include part of the emissions listed as process fugitives in Table 4-4.

Estimates of nonindustrial fugitive particulate emissions vary quite significantly in some cases. Cooper et al. (1979) estimated annual emissions from entrainment of dust from unpaved and paved roads at 290 x 10^6 metric tons and 7.2 x 10^6 metric tons, respectively. The U.S. Environmental Protection Agency (1980b) estimated emissions from the same categories at 35 x 10^6 metric tons and 4.7 x 10^6 metric tons, respectively. The differences can probably be attributed to the use of different assumptions and methods of calculation.

Finally, emission estimates by particle size and chemical composition also vary depending on the specific information and estimation method used. Most of these estimates are based on data from emissions sampling and analysis studies. Although these studies probably exhibit a high degree of accuracy on a case-by-case basis, data from a small number of individual sources should not be used to make generalizations. Emission characteristics, as well as emission quantities, are highly dependent on a number of source-specific factors, such as source and fuel characteristics and operating conditions. For example, the size distribution of particulate emissions from a given utility boiler can be altered significantly by changing the boiler load. Therefore, the emission characteristics from a particular source could vary from the information presented in this chapter.

4.3 NATURAL SOURCES AND EMISSIONS

Knowledge of natural sources and emissions of particulate matter and sulfur, including sulfur oxides, is important for understanding air pollution. Baseline concentrations in continental and marine air represent natural exposure levels and thus provide a reference for comparing concentrations in air polluted by emissions from manmade sources.

Significant natural sources of particulate matter and sulfur, including reduced sulfur which can become oxidized to sulfur oxides in the atmosphere (see Chapter 6), are terrestrial dust, sea spray, the biosphere, volcanoes, and wildfires. Estimates of emissions from these natural sources in the U.S. are described in more detail in subsequent sections. Table 4-2 presents a summary of natural source emission totals and characteristics.

4.3.1 Terrestrial Dust

Terrestrial dust is transferred to the atmosphere by the action of wind on the earth's soils and crustal materials. Theoretical and experimental studies (Gillette, 1974) indicate that sand grains, produced by the weathering of rocks and soils and moved by wind, cause the pulverization of soil minerals, as in sandblasting, to produce particles. These particles may become airborne and may be transported through the atmosphere for considerable distances. For example, dust from the Sahara Desert may be carried by air currents across the Atlantic Ocean as far as Florida and Barbados (Delany et al., 1967; Junge, 1957).

The amounts of global terrestrial dust have been estimated at 180 x 10^6 metric tons per year (Robinson and Robbins, 1971) and 100-500 x 10^6 metric tons per year[*] (National Research Council 1979). Calculations by Vandegrift et al. (1971), based on soil conservation data, resulted in estimated U.S. natural dust emissions of 57 x 10^6 metric tons per year.

Terrestrial dust in the atmosphere is composed primarily of seven major elements - silicon, aluminum, iron, sodium, potassium, calcium, and magnesium; organic material; and trace elements (Miller et al., 1972). The major elements are present in aerosol samples to nearly the same extent as in earth crustal material (Miller et al., 1972; Lawson and Winchester, 1979a). Atmospheric concentrations of many trace elements, however, are 10- to 1000-fold higher than would be expected from physical dispersion of soil materials. These anomalous trace element enrichments have been observed in many parts of the world, including northern Canada (Rahn, 1974), the South Pole (Zoller et al., 1974), and South America (Adams et al., 1977). Table 4-3 summarizes geometric mean enrichment factors, relative to aluminum, for various elements according to Rahn's compilation of all published data up to 1976 (Rahn, 1976).

The atmospheric enrichment sources of these elements are unknown, but transport from polluting industries (Rahn, 1974), natural rock volatility (Goldberg, 1976), and biogenic emanations (Barringer, 1977) have all been suggested. In general, not enough is known about element ratios in the natural atmosphere to detect a pollution component, thus a high anomalous content in particulate material cannot be related arbitrarily to air pollutants.

Most terrestrial dust particles are greater than 2 μm in diameter (U.S. Environmental Protection Agency, 1979). The major element constitutents of terrestrial dust also occur principally as coarse particles. Size-fractionated particle samples indicate that more than 90 percent of the mass occurs on the first three impactor stages, representing particle sizes of >4, 4-2, and 2-1 μm aerodynamic diameter (Winchester et al., 1979). The low relative abundance of submicron silicon, iron, and other major dust constituents reflects the greater

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[*] Includes unknown amounts of indirect manmade contributions.

TABLE 4-2. SUMMARY OF NATURAL SOURCE PARTICULATE AND SULFUR EMISSIONS[a]

Source category	Estimated U.S. emissions (10^6 metric tons per year)[b]		Particulate characteristics	
	Particulate	Sulfur[b]	Size range data	Chemical composition
Terrestrial dust	57	-	10% <1 μm	Al, Ca, Fe, K, Mg, Na, Si, organics, trace elements
Sea spray	5.5[c]	-	22% <3 μm	Seawater, organics
Biosphere	20	1.2 - 5.5[d]	Unknown	Organic aerosols, trace metals
Volcanoes	Variable	Variable	~5% <1 μm	Al, Ca, Fe, K, Mg, Si, Trace elements
Wildfires	0.5 - 1.0	-	80% <1 μm	Organics, trace minerals
TOTAL	~84+	~5+		

---

[a] All data are referenced in the text.

[b] When oxidized, one metric ton of sulfur equals 2 metric tons of sulfur dioxide, SO_2.

[c] Including 0.7 x 10^6 metric tons of sulfate aerosol.

[d] Predominantly reduced sulfur compounds.

TABLE 4-3. AEROSOL ENRICHMENT FACTORS RELATIVE TO Al

EF[a]	Elements
0.7-7	Li, Na, K, Rb
	Be, Mg, Ca, Sr, Ba
	Sc, Y, lanthanides
	Al, Ga, Tl
	Si, Ti, Zr, Hf, Th, U
	Mn, Fe, Co, Nb
	F, P
7-70[b]	Cr, Cs, V, W, B, Ni, Ge
70-400[b]	H, In, Cu, Mo, Bi, Zn, As
400-4000[b]	I, Hg, S, Cl, Au, Ag, Sn, Sb,
	Pb, Br, Cd, Te, Se, C, N

[a] Geometric means of element ratios to Al, relative to geochemical average earth crustal material.

$$EF = \frac{(\text{element/Al})_{\text{aerosol}}}{(\text{element/Al})\text{crust}}$$

[b] Anomalously enriched elements arranged in order of increasing EF.

Source: Based on Rahn (1976).

amount of energy needed in order for fine particles to be generated from soils by the wind-driven sandblasting mechanism. This energy is normally not provided by the atmosphere near the ground.

4.3.2 Sea Spray

Aerosol droplets are generated at the ocean surface by the action of wind, principally through a process whereby air bubbles become entrained and rise to burst at the surface. Robinson and Robbins (1971) estimated global emissions of particles from sea spray at 900 x 10^6 metric tons per year, including 120 x 10^6 metric tons of sulfate aerosol per year (Eriksson, 1959, 1960; Robinson and Robbins, 1968). Assuming 10 percent of the annual production penetrates continental areas (Eriksson, 1959), and assuming the impact on the U.S. is proportional to the ratio of the U.S. to global coastline (12 x 10^3 miles: 200 x 10^3 miles), approximately 5.5 x 10^6 metric tons of sea spray particulate per year (including 0.7 x 10^6 metric tons of sulfate aerosol per year) impact on U.S. coastal areas.

Sea spray is composed of seawater, organic materials, and surface-active materials which may be concentrated into the 0.05 to 0.5 µm thickness of bubble surface (MacIntyre, 1974). The surface-active material may be of natural or pollutant origin and may include organic molecular films and organic and inorganic particles including viruses, bacteria, and other microscopic organisms (Blanchard and Parker, 1977; Duce and Hoffman, 1976). Such materials, by becoming components of sea spray aerosol droplets, may be carried through the atmosphere far from the point of origin. The potential for virus transfer from coastal waters to the atmosphere and transport by winds inland to inhabited areas has been demonstrated (Baylor et al., 1977), although the process is not clearly understood.

Because of differences in the mechanics of droplet formation, differences in chemical composition may exist (Berg and Winchester, 1978). For example, some droplets may or may not contain the surface-active particulate matter scavenged from the water column by the rising bubbles. Chloride, bromide, and iodide also may be present (Moyers and Duce, 1972a,b). The general processes through which sea spray droplets are formed and transported have been described by a number of authors, including Blanchard and Woodcock (1957) and Wallace and Hobbs (1977). The size distribution of sea spray particles by weight percent, as documented by Taback et al. (1979), is as follows: >10 µm, 24 percent; 3-10 µm, 54 percent; 1-3 µm, 20 percent; <1 µm, 2 percent.

4.3.3 Biogenic Emanations

Plants emit particulate matter in the form of organic aerosols, trace metals, and nutrients. Global emissions of volatile organic compounds released from plants have been estimated at 200 x 10^6 metric tons per year (Went, 1960). The U.S. total would probably be less than 20 x 10^6 metric tons per year. Isoprene derivatives such as terpenes, caroteniods, and other compounds are believed to predominate and are likely to be partially oxidized, resulting in blue haze and submicron condensation nuclei (Went, 1960; Went et al., 1967; Rasmussen and Went, 1965; Schnell and Vali, 1972, 1973).

Trace metals have long been known to occur in fluids secreted by plants. Radiotracer strontium is transferred from plant foliage to the atmosphere, presumably in particles (Moorby and Squire, 1963) which may be affected by electric fields (Fish, 1972). Transpiration causes the transfer of both cations and anions to the atmosphere (Nemeryuk, 1970). Twenty-seven trace elements have been identified in exudates from coniferous trees (Curtin et al., 1974). Radiotracer experiments using zinc and lead show that particles greater than 5 μm in diameter contain most of the metals released (Beauford et al., 1975, 1977). Sulfur, potassium, and phosphorus have also been associated with tropical forests and occur in large aerosol particles (Lawson and Winchester, 1979b). The metal content of plant-derived aerosols is so high that several investigators suggest that it might serve as an indicator for geochemical prospecting (Barringer, 1977; Curtin et al., 1974).

The terrestrial and marine biospheres, while not direct sources of sulfur dioxide, are significant sources of reduced sulfur compounds. Volatile reduced sulfur compounds are released to the atmosphere via microbiological processes and may become oxidized to SO_2 and sulfate. The compounds released included hydrogen sulfide (H_2S), dimethyl sufide (DMS), dimethyl disulfide (DMDS), carbon disulfide (CS_2), carbonyl sulfide (COS), and methyl mercaptan (CH_3SH) (Lovelock et al., 1972; Rasmussen, 1974; Lovelock, 1974; Adams et al., 1979a). Transformation to H_2S and thence to SO_2 and $SO_4^=$ is predicted (McElroy et al., 1980), as well as direct oxidation to SO_2 and/or SO_4.

The classic method of estimating biogenic sulfur emissions has been to identify the net difference between input from known sources and removal by scavenging processes as being indicative of an unmeasured source, namely a widespread source in the biosphere. A number of previous estimates of global emissions of reduced sulfur compounds range from 64 x 10^6 metric tons per year (land) and 27 x 10^6 metric tons per year (ocean) (Robinson and Robbins, 1968) to 3 x 10^6 metric tons per year (land) and 34 x 10^6 metric tons per year (ocean) (Granat et al., 1976). Granat's estimate, scaled down to the U.S., would result in 0.2 x 10^6 metric tons per year (land) and about 2-5 x 10^6 metric tons per year (ocean) (based on Galloway and Whelpdale, 1980). These estimates, however, were derived indirectly as balances for other sulfur fluxes.

Results of recent field monitoring studies conducted by Maroulis and Bandy (1977), McClenny et al. (1979), and Adams et al. (1979a) yield slightly different estimates. Adams et al. (1979b) calculated a mean annual sulfur flux of 0.02 g S $m^{-2}yr^{-1}$, weighted over a number of Eastern U.S. soil types, including marshes. The entire U.S. would probably average 0.02-0.05 g S $m^{-2}yr^{-1}$ (Adams, 1980). When these numbers are applied to the entire earth's land area (about 56 million square miles) the result is about 3-7 x 10^6 metric tons per year. The land area of the U.S. (3.6 million square miles) emits about 0.2-0.5 x 10^6 metric tons per year based on 0.02-0.05 g S $m^{-2}yr^{-1}$. The impact of marine biogenic activity would be limited primarily to coastal areas. Sulfur emissions from marine biogenic activity are probably on the order of 1 x 10^6 metric tons per year (based on Galloway and Whelpdale, 1980). These lower estimates of sulfur emissions on a national scale do not preclude significant localized biogenic sulfur emissions, especially in areas where wetlands are prevalent (Henry and Hidy, 1980). Marshes and tidal flats may have high local sulfur-gas production (Hitchcock, 1976; Hitchcock et al., 1980), but since the total area in the U.S. covered by such features is relatively small, the contribution to total background sulfur is modest. Thus, the inventory of terrestrial biogenic sulfur emission should not overemphasize the wetland areas as a source. In the western U.S., more arid soils would be expected to have a much reduced sulfur emission rate, but detailed study in this area is lacking.

4.3.4 Volcanic Emissions

Emissions from volcanic eruptions and fumaroles may contribute to global atmospheric background levels of particulate matter and sulfur. Volcanoes are one of the few sources of atmospheric particles and sulfur whose effects can be felt at great distances. Plumes from volcanoes intense enough to inject material into the upper troposphere or lower stratosphere (about 10 to 15 miles above the earth's surface) have been tracked great distances before removal (Fegley et al., 1980). The famous eruption of Krakatoa in 1883 injected enough dust and sulfur into the stratosphere to cause brilliant sunsets thousands of kilometers away and a global reduction of incoming solar radiation (Wexler, 1951a,b).

Until recently, volcanic activity has been relatively insignificant in the United States. The Mt. St. Helens eruption was only the second this century in the contiguous United States. Mt. Lassen, California, in 1915, was the first. About 20 volcanic eruptions have occurred in Hawaii and Alaska since 1900.

With the 1980 eruption of Mt. St. Helens in the Pacific northwest, considerable attention has been focused on the potential impact of volcanoes on the atmosphere and air quality. Away from the immediate downwind area, volcanic impacts can probably be related to a cycle that starts with injection into the stratosphere of dust and sulfur gases, oxidation and reaction of the sulfur to form particulate compounds, and finally injection of the particles into the troposphere, where they are scavenged. Since injection from the stratosphere occurs mainly in low pressure systems, it is likely that precipitation scavenging predominates.

The average global volcanic emission rates of particles and sulfur compounds have been estimated by a number of investigators. Robinson and Robbins (1971) estimated the average global emission rate of small particles (the persistent fraction) at 3.6×10^6 metric tons per year. Airborne measurements and observations made during the 1976 eruption of the St. Augustine volcano (Alaska) led to particulate emissions estimates for a 1-year period for that particular volcano of 6×10^6 metric tons for particles of 0.01 to 66 μm in size and 0.25×10^6 metric tons for particles 0.01 to 5 μm in size (Stith et al., 1978).

Estimates of global volcanic sulfur emissions, as documented by Granat et al. (1976), range from 0.75 to 3.75×10^6 metric tons per year. Emissions of SO_2 for a 1-year period at St. Augustine were estimated at 0.1×10^6 metric tons (or 0.05×10^6 metric tons of sulfur) (Stith et al., 1978). The St. Augustine volcano also emitted lesser quantities of H_2S. Stith et al. (1978) estimated global volcanic emissions of H_2S at 1×10^6 metric tons per year.

Particles collected from the St. Augustine eruptions were composed primarily of silicon, aluminum, magnesium, calcium, and iron. Trace amounts of potassium, titanium, and sulfur were also present (Stith et al., 1978). Samples of Mt. St. Helens ash contained mainly silicon, aluminum, iron, calcium, sodium, magnesium, and potassium. Titanium, phosphorus, and manganese, as well as traces of sulfur, chlorine, strontium, barium, vanadium, zirconium, and zinc (among others) were also found (Fruchter et al., 1980).

Based on the St. Augustine particulate emissions (6×10^6 metric tons total, 0.25×10^6 metric tons less than 5 μm), less than 5 percent of the particles were smaller than 5 μm in size (Stith, et al., 1978). According to preliminary airborne studies of Mt. St. Helens ash, significant amounts of particulate matter between 1 and 2 μm have been emitted to the atmosphere (Hobbs et al., 1981). Other preliminary studies of Mt. St. Helens ash place the fraction less than 3.5 μm at around 2 percent (Fruchter et al., 1980).

4.3.5 Wildfires

The three major types of large scale fires are: wildfires, prescription fires in natural areas, and agricultural burning. The latter two types are exclusively caused by human activities. Wildfires, defined by the U.S. Department of Agriculture Forest Service as "any fire that burns uncontrolled in vegetative or associated flammable material," are treated here, as in the literature, as a natural emission source even though man's activities cause about 90 percent of their total number; only 10 percent are truly "natural," resulting from lightning (U.S. Department of Agriculture, Forest Service, 1979).

Wildfire particulate emissions calculations typically have been based on three numbers: wildfire acreage, fuel burned per acre, and emissions per unit mass of fuel. Robinson and Robbins (1971) estimated yearly particulate emissions from forest fires in the U.S. as 0.7×10^6 metric tons, based on 4.5×10^6 acres burned, 18 tons of fuel per acre, and 17 pounds of particulate per ton of fuel. Yamate (1973) arrived at 0.5×10^6 metric tons per year, assuming numbers similar to those used by Robinson and Robbins.

In recent research, however, particulate emissions per unit mass of fuel were estimated at 17-67 pounds per ton (GEOMET, 1978) and 80 pounds per ton (Radke et al., 1978), based on airborne sampling studies in Oregon and Washington. Because emissions from fires are dependent on fuel conditions and fire behavior (GEOMET, 1978), the estimates should probably be averaged. If an emission rate of 40 pounds per ton, a U.S. wildfire acreage of 3.15×10^6 in 1977 (U.S. Department of Agriculture, Forest Service, 1979), and a U.S. average of 17 tons of fuel per acre (Yamate, 1973) are assumed, U.S. particulate emissions from wildfires total 1.0×10^6 metric tons per year.

Chemical analysis of particulate matter from temperate forest burning indicates approximately 50 percent benzene-soluble organic matter, 40 percent elemental carbon, and 10 percent mineral matter (Ryan and McMahon, 1976). Another analysis suggests 55 percent tar, 25 percent soot, and 20 percent ash (Vines et al., 1971). About 80 percent of the mass of smoke particles from forest fires is less than 1 μm in diameter, with the average size being 0.1 μm (GEOMET, 1978; Radke et al., 1978; Vines et al., 1971).

Wildfires contribute varying amounts of other pollutants to the atmosphere. Carbon monoxide and hydrocarbons are the most significant. Wildfires are not, however, considered to be a source of sulfur oxides (Radke et al., 1978; Yamate, 1973; Vines et al., 1971).

4.4 MANMADE SOURCES AND EMISSIONS

A number of definable source categories emitting particulate matter and sulfur oxides can be attributed solely to man and are the subjects of this section. Representative estimates of emissions from these source categories in the United States are summarized in Table 4-4. Manmade emissions of particulate matter result primarily from stationary point sources (fuel combustion and industrial processes), industrial process fugitive particulate emission sources, nonindustrial fugitive sources (e.g., roadway dust from paved and unpaved roads, wind erosion of cropland), and transportation sources (e.g., automobiles). The data in Table 4-4 show that nonindustrial fugitive emissions are significant on a mass basis. However, the relative impact of these emissions is somewhat lessened by their coarse size and the fact that fugitive dust sources (e.g. unpaved roads) are more prevalent in rural areas.

TABLE 4-4. SUMMARY OF ESTIMATED ANNUAL MANMADE EMISSIONS (1978)

Source category	Emissions (10^6 metric tons) Particulate matter	Sulfur oxides
Stationary point sources	10.5	26.2
Industrial process fugitives	3.3[a]	-
Nonindustrial fugitives	110-370	-
Transportation sources	1.3	0.8
TOTAL	~125-385	27.0

[a] NOTE: Approximately half of the 3.3 x 10^6 metric tons of particulate matter from process fugitives are probably included in the 10.5 x 10^6 metric tons from stationary point sources. See Section 4.2 for explanation.

Source: U.S. Environmental Protection Agency, 1980a

Manmade emissions of sulfur oxides result almost exclusively from stationary point sources. The combustion of fossil fuels by electric utilities causes most sulfur oxide emissions. Transportation sources also contribute a small amount of sulfur oxide emissions.

4.4.1 Historical Emission Trends

Economic conditions and the degree to which air pollution control devices are used are the two factors having the most impact on emissions totals, especially from stationary point sources (fuel combustion and industrial processes). Economic conditions affect the amounts of goods produced and, therefore, the amounts of emissions generated. The economics of relative fuel prices also affect emissions; that is, higher prices on oil and natural gas cause increased use of coal, which generally emits more particulate matter and sulfur oxides per unit energy than oil or natural gas. Increased use of control devices has resulted from the enactment of regulations such as New Source Performance Standards and State Implementation Plans.

Historical trends in emissions of particulate matter (not including fugitive emissions, which have not been documented) and sulfur oxide are shown in Table 4-5. Data for the years 1940, 1950, and 1960 are from the U.S. Environmental Agency (1978b); data for 1970 through 1978 are from the U.S. Environmental Protection Agency (1980a). Emissions estimates from the latter are considered more accurate. It should be noted that local emission trends might not necessarily coincide with national emission trends.

Nationwide emissions of particulate matter (not including fugitive emissions) have generally decreased since 1950 after a slight increase from 1940 to 1950. These emissions have resulted primarily from stationary fuel combustion (utility and industrial) and industrial processes. Particulate emissions from stationary fuel combustion decreased fairly consistently from 1940 to 1978. From 1940 through the early 1970's this decrease was probably due to increased use of oil and natural gas. Even though the oil embargo of 1973-74 caused increased use of coal, conservation efforts by industry and the installation of control equipment resulted in further reductions in particulate emissions through 1978.

Industrial process emissions of particulate matter increased from 1940 to 1960, then declined steadily through 1978. Increases were attributed to expanding production; decreases were attributed to installation of controls.

Nationwide emissions of sulfur oxides have increased overall since 1940. As with particulate matter, stationary fuel combustion (primarily utility and industrial) and industrial processes (primarily ore smelting) have been the main contributors. Coal combustion was the largest stationary fuel combustion source, although coal use by industrial, commercial/institutional, and residential users has declined, corresponding with a decrease in sulfur oxide emissions from those categories. Increased coal use by electric utilities has more than offset this decrease. Sulfur oxide emissions from electric utilities account for more than half the total emissions. Flue gas desulfurization (FGD) systems have seen only limited use to date and have not had a major impact on emissions. About 11 percent of U.S coal-fired electrical generating capacity is presently fitted with FGD (U.S. Environmental Protection Agency, 1980c).

Increased industrial production caused most of the sulfur oxide emission increases through 1970. Since that time, however, significant emission reductions from nonferrous smelters and sulfuric acid plants have occurred. For smelters, byproduct recovery of sulfuric acid has significantly reduced sulfur oxide emissions. Sulfur oxide emissions from copper, lead and zinc smelters have decreased from 4 x 10^6 metric tons per year in 1970 to about 2 x 10^6 metric tons per year in 1978.

Future emission trends are subject to a number of assumptions concerning economic climate, fuel use, environmental policy, and control technology. These considerations are beyond the scope of this document. (See U.S. Department of Energy, 1978; 1979.)

TABLE 4-5 (a). NATIONAL ESTIMATES OF PARTICULATE EMISSIONS[a]
(10^6 metric tons per year)

SOURCE CATEGORY	1940	1950	1960	1970	1975	1978
Stationary fuel combustion	8.7	8.1	6.7	7.2	5.1	3.8
Industrial processes	9.9	12.6	14.1	12.8	7.4	6.2
Solid waste disposal	0.5	0.7	0.9	1.1	0.5	0.5
Transportation	0.5	1.1	0.6	1.1	1.0	1.3
Miscellaneous[b]	5.2	3.7	3.3	1.0	0.6	0.7
TOTAL	24.8	26.2	25.6	23.2	14.6	12.5

Table 4-5 (b). NATIONAL ESTIMATES OF SULFUR OXIDE EMISSIONS
(10^6 metric tons per year)

SOURCE CATEGORY	1940	1950	1960	1970	1975	1978
Stationary fuel combustion	15.1	16.6	15.7	22.7	20.9	22.1
Industrial processes	3.4	4.1	4.8	6.2	4.5	4.1
Solid waste disposal	0.0	0.1	0.0	0.1	0.0	0.0
Transportation	0.6	0.8	0.5	0.7	0.8	0.8
Miscellaneous[b]	0.4	0.4	0.4	0.1	0.0	0.0
TOTAL	19.5	22.0	21.4	29.8	26.2	27.0

[a] Does not include industrial process fugitive particulate emissions, and non-industrial fugitives from paved and unpaved roads, wind erosion, construction activities, agricultural tilling, and mining activities.

[b] Includes forest fires, agricultural burning, coal refuse burning, and structural fires.

Sources: U.S. Environmental Protection Agency (1978b)
U.S. Environmental Protection Agency (1980a)

4.4.2 Stationary Point Source Emissions

In this analysis of sources and characteristics of particulate and sulfur oxide emissions from stationary point sources, the two major source categories are fuel combustion and industrial processes. A third but minor category is solid waste disposal. Table 4-6 lists calculated estimates of 1978 emissions from these source categories. Based on these estimates, fuel combustion contributed 36 percent of the particles and 84 percent of the sulfur oxides emitted by stationary point sources in 1978. Industrial processes emitted 59 percent of the particulate matter and 16 percent of the sulfur oxides. Solid waste disposal contributed 5 percent of the particulate matter.

TABLE 4-6. 1978 ESTIMATES OF PARTICULATE AND SULFUR OXIDE EMISSIONS FROM STATIONARY POINT SOURCES

Source category	Emissions (10^3 metric tons) Particulate Matter	 Sulfur oxides
Fuel combustion		
Utility		
Coal	2,350	15,900
Oil	140	1,720
Gas	10	0
Industrial		
Coal	700	1,890
Oil	90	1,150
Gas	40	0
Other fuels[a]	280	150
Commercial/Institutional		
Coal	20	40
Oil	60	900
Gas	10	0
Residential		
Coal	20	60
Oil	20	260
Gas	30	0
Industrial processes		
Metals		
Iron and steel	830	110
Primary smelting	480	1,960
Iron foundries	140	0
Other	120	0
Mineral products		
Cement	780	670
Asphalt	150	0
Lime	150	0
Crushed rock	1,340	0
Other	910	30
Petroleum		
Refining	70	900
Natural gas production	0	140
Chemicals		
Sulfuric acid	0	220
Other	190	0
Other		
Grain processing	730	0
Pulp and paper	240	80
Other	60	0
Solid waste disposal	500	0
TOTAL	10,460	26,180

[a] Primarily wood/bark waste.

Source: U.S. Environmental Protection Agency (1980a).

An unknown percentage of particulate matter and sulfur oxides is emitted as primary sulfates. Primary sulfates consist of gaseous sulfur trioxide (SO_3), sulfuric acid (H_2SO_4), and particulate sulfates. These primary sulfates are of increasing concern because of their potential impacts, especially on health, but estimates of primary sulfate emission quantities from major sources have not been generated to date. Secondary sulfates can be formed in the atmosphere, following oxidation of SO_2, hours or even days after its release. The principal reactions are described in Chapter 2; field measurements attempting to trace the actual production and fate of secondary sulfates under the complex influences and diverse combinations of meteorological variables are discussed in Chapter 6.

Varying amounts of particulate matter and sulfur oxides are emitted in different geographic regions of the United States. Table 4-7 presents State and regional estimates of 1979 population, PM and SO_x emissions (based on the 1977 NEDS inventory), emission densities, and percentage contributions to total U.S. point source emissions. Based on this information, Regions III through VI accounted for over 70 percent of the particulate matter and sulfur oxides emitted by stationary sources in the U.S. In Region III, utility and industrial fuel combustion contributed most of the particulate matter and sulfur oxides. The mineral products industry also contributed heavily to particulate emissions. In Regions IV and V, utility fuel combustion and the mineral products industry contributed most of the particulate emissions, while utility fuel combustion contributed most of the sulfur oxide emissions. The mineral products industry and total fuel combustion caused most of the particulate emission in Region VI. The primary metals and petrochemical industries, along with fuel combustion, contributed most of the sulfur oxides emissions in Region VI.

In other regions grain processing (Region VII) and mineral products (Region IX) emitted large amounts of particulate matter. Fuel combustion (Regions II and VII) and the primary metals industry (Region IX) contributed significant amounts of sulfur oxides.

Several factors affect the quantity and characteristics (size and composition) of particulate matter emissions from stationary sources. Examples of such factors are source type, operating conditions and practices, fuel characteristics (if the source is a fuel combustion source), and type of emission control equipment, if any. The chemical composition of emitted particles can determine possible reactions that occur during transport and the final effects upon receptors (see Chapters 5 and 6). Particle size affects suspension time and transport distance and is also an important factor in determining any possible health effects (see Chapters 11-14).

Table 4-8 presents a summary of particle size and chemical composition data for uncontrolled particulate emissions from stationary sources. These data demonstrate the strong influence of control devices on the particle size distribution of emissions. Table 4-9 illustrates that, for coal-fired boilers, most control devices are more efficient at removing larger particles. Therefore, even though the total mass of smaller particles decreases, the percentage increases. [Refer to U.S. Environmental Protection Agency (1980b) for further

TABLE 4-7. STATE-BY-STATE LISTING OF TOTAL PARTICULATE AND SULFUR OXIDE EMISSIONS FROM STATIONARY POINT SOURCES (1977),[a] POPULATION, AND DENSITY FACTORS

Region and state	Population[b] (1000's)	Total area[c] (mi^2)	Population density (people/mi^2)	Particulate matter			Sulfur oxides		
				Total emissions (10^3 metric tons)	Emission density (tons/mi^2)	State emissions (% of U.S.)	Total emissions (10^3 metric tons)	Emissions density (tons/mi^2)	State emissions (% of U.S.)
Region I									
Connecticut	3,099	5,009	619	17.6	3.5	0.25	53.4	10.7	0.20
Maine	1,091	33,215	33	37.7	1.1	0.54	115.2	3.5	0.44
Massachusetts	5,774	8,257	704	38.2	4.6	0.55	206.7	25.0	0.78
New Hampshire	871	9,304	94	7.7	0.8	0.11	100.8	10.8	0.38
Rhode Island	935	1,214	770	1.7	1.4	0.02	10.2	8.4	0.04
Vermont	487	9,609	51	2.2	0.2	0.03	0.9	0.1	<0.01
TOTAL	12,257	66,608	184	105.2	-	-	487.3	-	-
Percent of U.S.	5.5	1.8	-	1.51	-	-	1.85	-	-
Region II									
New Jersey	7,327	7,836	935	46.8	6.0	0.67	213.7	27.3	0.81
New York	17,748	49,576	358	171.6	3.5	2.46	749.7	15.1	2.85
Puerto Rico	2,712	3,435	790	55.2	16.1	0.79	280.1	81.5	1.06
Virgin Island	62	133	466	11.3	84.6	0.16	3.6	27.4	0.01
TOTAL	27,849	60,980	457	284.9	-	-	1,247.2	-	-
Percent of U.S.	12.6	1.7	-	4.08	-	-	4.73	-	-
Region III									
Delaware	582	2,057	283	31.0	15.1	0.44	115.5	56.2	0.44
District of Columbia	674	67	10,060	1.7	25.1	0.02	15.0	223.5	0.06
Maryland	4,144	10,577	392	40.3	3.8	0.58	289.2	27.3	1.10
Pennsylvania	11,862	45,333	259	652.9	14.4	9.36	2,149.5	47.4	8.16
Virginia	5,032	40,817	126	101.9	2.5	1.46	372.0	9.1	1.41
West Virginia	1,821	24,181	77	174.4	7.2	2.50	1,084.7	44.9	4.12
TOTAL	24,143	123,032	196	1,002.2	-	-	4,025.8	-	-
Percent of U.S.	10.9	3.4	-	14.36	-	-	15.28	-	-

TABLE 4-7. (continued)

Region and state	Population[b] (1000's)	Total area[c] (mi^2)	Population density (people/mi^2)	Particulate matter			Sulfur oxides		
				Total emissions (10^3 metric tons)	Emission density (tons/mi^2)	State emissions (% of U.S.)	Total emissions (10^3 metric tons)	Emissions density (tons/mi^2)	State emissions (% of U.S.)
Region IV									
Alabama	3,742	51,609	73	248.5	4.82	3.56	898.0	17.4	3.41
Florida	8,594	58,560	147	182.5	3.12	2.62	861.6	14.7	3.27
Georgia	5,084	58,876	86	88.6	1.50	1.27	597.5	10.1	2.27
Kentucky	3,498	40,395	87	369.1	9.14	5.29	1,442.4	35.7	5.48
Mississippi	2,404	47,716	50	135.8	2.9	1.95	211.1	4.4	0.80
North Carolina	5,577	52,586	106	159.6	3.02	2.29	510.6	9.7	1.94
South Carolina	2,918	31,055	94	79.1	2.6	1.13	260.7	8.4	0.99
Tennessee	4,357	42,244	103	132.3	3.13	1.90	1,135.3	26.9	4.31
TOTAL	36,174	383,041	94	1,395.5	-	-	5,917.1	-	-
Percent of U.S.	16.4	10.6	-	20.0	-	-	22.46	-	-
Region V									
Illinois	11,243	56,400	199	448.5	8.0	6.43	1,462.1	25.9	5.55
Indiana	5,374	36,291	148	313.4	8.6	4.49	1,572.9	43.3	5.97
Michigan	9,189	58,216	158	209.3	3.6	3.00	1,064.0	18.3	4.04
Minnesota	4,008	84,068	48	116.5	1.4	1.67	231.6	2.8	0.88
Ohio	10,749	41,222	261	529.3	12.8	7.58	2,840.6	68.9	10.78
Wisconsin	4,679	56,154	83	231.8	4.1	3.32	569.8	10.1	2.16
TOTAL	45,242	332,351	136	1,848.8	-	-	7,740.1	-	-
Percent of U.S.	20.5	9.2	-	26.49	-	-	29.38	-	-
Region VI									
Arkansas	2,186	53,104	41	105.8	2.0	1.52	103.1	1.9	0.39
Louisana	3,966	48,523	82	295.7	6.1	4.24	290.4	6.0	1.10
New Mexico	1,212	121,666	10	77.6	0.6	1.11	511.8	4.2	1.94
Oklahoma	2,880	69,919	41	71.0	1.0	1.02	91.1	1.3	0.35
Texas	13,014	267,338	49	367.1	1.4	5.26	1,141.8	4.3	4.33
TOTAL	23,258	560,550	41	917.2	-	-	2,138.3	-	-
Percent of U.S.	10.5	15.5	-	13.14	-	-	8.12	-	-

TABLE 4-7. (continued)

				Particulate matter			Sulfur oxides		
Region and state	Population[b] (1000's)	Total area[c] (mi^2)	Population density (people/mi^2)	Total emissions (10^3 metric tons)	Emission density (tons/mi^2)	State emissions (% of U.S.)	Total emissions (10^3 metric tons)	Emissions density (tons/mi^2)	State emissions (% of U.S.)
Region VII									
Iowa	2,896	56,290	51	192.0	3.4	2.75	288.9	5.1	1.10
Kansas	2,348	82,264	29	157.8	1.9	2.26	157.4	1.9	0.60
Missouri	4,860	69,686	70	112.4	1.6	1.61	1,296.1	18.6	4.92
Nebraska	1,565	77,227	20	110.1	1.4	1.58	41.5	0.5	0.16
TOTAL	11,669	285,467	41	572.3	-	-	1,783.9	-	-
Percent of U.S.	5.3	7.4	-	8.20	-	-	6.77	-	-
Region VIII									
Colorado	2,670	104,247	26	34.2	0.3	0.49	91.4	0.9	0.35
Montana	785	147,138	5	22.8	0.2	0.33	177.7	1.2	0.67
North Dakota	652	70,665	9	19.2	0.3	0.28	97.3	1.4	0.37
South Dakota	690	77,047	9	37.3	0.5	0.53	34.6	0.4	0.13
Utah	1,307	84,916	15	72.3	0.9	1.04	173.6	2.0	0.66
Wyoming	424	97,914	4	144.4	1.5	2.07	146.4	1.5	0.56
TOTAL	6,528	581,927	11	330.2	-	-	721.0	-	-
Percent of U.S.	3.0	16.1	-	4.73	-	-	2.74	-	-
Region IX									
Arizona	2,354	113,909	21	40.1	0.4	0.58	1,097.9	9.6	4.17
California	22,294	158,693	140	185.7	1.2	2.66	498.0	3.1	1.89
Hawaii	897	6,450	139	15.8	2.5	0.23	55.6	8.6	0.21
Nevada	660	110,540	6	85.3	0.8	1.22	295.2	2.7	1.12
Guam	85	212	401	4.5	21.3	0.06	53.6	252.9	0.20
TOTAL	26,317	389,880	68	331.5	-	-	2,000.4	-	-
Percent of U.S.	11.9	10.8	-	4.75	-	-	7.59	-	-

TABLE 4-7. (continued)

Region and state	Population[b] (1000's)	Total area[c] (mi^2)	Population density (people/mi^2)	Particulate matter: Total[a] emissions (10^3 metric tons)	Particulate matter: Emission density ($tons/mi^2$)	Particulate matter: State emissions (% of U.S.)	Sulfur oxides: Total[a] emissions (10^3 metric tons)	Sulfur oxides: Emissions density ($tons/mi^2$)	Sulfur oxides: State emissions (% of U.S.)
Region X									
Alaska	403	589,757	1	12.7	<0.1	0.18	5.6	<0.1	0.02
Idaho	878	83,557	11	15.1	0.2	0.22	34.2	0.4	0.13
Oregon	2,444	96,981	25	67.1	0.7	0.96	23.3	0.2	0.09
Washington	3,774	68,192	55	96.2	1.4	1.38	217.5	3.2	0.83
TOTAL	7,499	838,487	9	191.0	-	-	280.7	-	-
Percent of U.S.	3.4	23.0	-	2.74	-	-	1.07	-	-
U.S. TOTALS	220,951	3,620,000	61	6,978.7			26,341.8		

[a] Source: U.S. Environmental Protection Agency (1980b). The accuracy of these data may not warrant the number of significant figures shown.

[b] Source: U.S. Department of Commerce (1979).

[c] Source: The World Almanac and Book of Facts 1980 (1980).

TABLE 4-8. EXAMPLES OF UNCONTROLLED PARTICULATE EMISSION CHARACTERISTICS

Source category	Particle size data[a] (weight % less than stated size) 15 μm	2.5 μm	1.0 μm	Chemical composition data[b] Major elements and compounds	Trace elements (less than 1% by weight)
Fuel combustion					
Utility					
Coal	15-90	5-70	1-15	Al,Ca,Fe,Si, sulfates,organics	As,B,Ba,Be,Cd,Cl,Co,Cr, Cu,F,Hg,K,Mg,Mn,Na,Ni, P,Pb,S,Se,Ti,V,Zn,Zr
Oil	95	70-95	5-20	Al,Ca,Fe,Mg,Na, sulfates,organics	As,Ba,Br,Co,Cr,Cu,K, Mn,Mo,Ni,Pb,Se,Sr,Ti,V
Industrial					
Oil	--	--	65-95	Al,Fe,Mg,Si, sulfates,organics	As,Ba,Ca,Cd,Co,Cr,Cu,Hg, K,Mo,Ni,Ph,Se,Sr,Ti,V,Zn
Gas	--	--	100	Cl,Na,sulfates, organics	--
Commercial/Institional/ Residential					
Oil	--	--	--	Al,Ca,Mg,Zn, sulfates	As,Ba,Cd,Cr,Cu,Hg,K, Ni,Pb,Sb,C
Gas	--	--	100	Cl,Na,sulfates organics	--

TABLE 4-8. (continued)

Source category	Particle size data[a] (weight % less than stated size) 15 µm	2.5 µm	1.0 µm	Chemical composition data[b] Major elements and compounds	Trace elements (less than 1% by weight)
Industrial processes					
Metals					
Iron and steel	--	35-99	30-95	Al,C,Ca,Cr,Fe,K,Mg, Mn,Pb,Si,Zn, sulfates,organics	Ag,As,Br,Cd,Cs,Cu,F,I, Mo,Ni,Rb,Se,Sn,Sr,V,Zr
Primary aluminum	90	75	35-45	Al,C,Ca,F,Fe,Na	--
Primary copper	--	20-95	70	Cu,Pb,S,Zn	Ag,Al,As,Cd,Hg,Sb,Se, Si,Te
Primary lead	--	80	--	Pb,Zn	As,Cd,Se,Te
Primary zinc	--	90-98	--	Cd,Fe,Pb,S,Zn	Cu,Hg,Mn,Sn
Iron foundries	70-95	65-90	65	--	--
Mineral products					
Cement	80	30	5-30	Al,C,Ca,Cl,K,Mg, Na,Si,carbonates, sulfates	Ag,Ba,Cd,Cr,Cu,F,Fe,Mn, Mo,Ni,Pb,Rb,Se,Ti,Zn
Asphalt	10-15	1-2	< ½	Al,C,Ca,Fe,K,Mg, Si,sulfates	Ag,As,Ba,Cr,Ti
Lime	--	25-50	5	Ca,Fe,Mg,Se,Si, carbonates	--
Gypsum	--	--	20	Al,C,CA,Mg,Na, sulfates	As,Ba,Br,Cd,Cl,Cr,Cu, Fe,K,Mn,Mo,Ni,Pb,Se, Sr,Y.Zn

TABLE 4-8. (continued)

	Particle size data[a]			Chemical composition data[b]	
	(weight % less than stated size)				
Source category	15 μm	2.5 μm	1.0 μm	Major elements and compounds	Trace elements (less than 1% by weight)
Crushed rock	--	--	1-2	Ca,Si,P	Ba,Cu,Fe,K,Mn,Sr
Petroleum	--	--	50-90	Asphalt, coke dust, sulfuric acid mist, flyash, soot	--
Chemicals					
sulfuric acid	--	40-95	10-55	Sulfuric acid mist	--
Others					
Grain processing	15	1	0	Organics	--
Pulp and paper	90-95	70-80	--	Ca,Mg,Na,carbonates, sulfates	--
Solid waste disposal					
Incinerators	45	35	--	--	--

[a] Since a number of references were cited, some characterizing different processes, discrepancies may exist in the ranges shown.

[b] Elements and compounds listed were included in at least one of the references cited.

Sources: Surprenant et al. (1979); Taback et al. (1979); U.S. Environmental Protection Agency (1980c); U.S. Environmental Protection Agency (1980d); Plemons and Parnell (1981).

TABLE 4-9. SIZE-SPECIFIC PARTICULATE EMISSIONS FROM COAL-FIRED BOILERS

Control device	Inlet size distribution (uncontrolled) (Mass percent less than)		Outlet size distribution (controlled) (Mass percent less than)		Removal efficiency (%)		
	15 μm	2.5 μm	15 μm	2.5 μm	(at) 15 μm	2.5 μm	overall
ESP	15-50	5-20	70-95	15-70	65-99+	60-95	85-99+
Wet scrubber	30-95	10-70	80-95	50-90	75-95	50-90	80-95
Fabric filter[a]	55-65	20-45	~80	20-90	~99	~99	~99

[a] Based on limited data.

Source: U. S. Environmental Protection Agency (1980d).

discussion on the effects of control devices on emissions characteristics.] Therefore, the application of the particle size percentages representing uncontrolled emissions shown in Table 4-8 to the emission quantities from controlled sources listed in Tables 4-6 and 4-7 would probably result in an underestimation of the finer particle fractions.

As a further example of the difference between controlled and uncontrolled conditions, control devices have helped reduce the mass flow of particulate emissions in California's South Coast Air Basin by 95 percent or more from what prevailed under uncontrolled conditions. However, over 90 percent of the remaining emissions (both point sources and miscellaneous area sources) have particle sizes less than 10 μm (Taback et al., 1979).

A final point with respect to Table 4-8 is that the particle size and chemical composition data represent an overall source category. Therefore, in the iron and steel industry, for example, not all of the many different processes emitting particulate matter would necessarily have emissions exhibiting the exact characteristics shown. Further information can be obtained from the cited documents.

The same factors mentioned earlier may affect the quantity and characteristics of sulfur oxide emissions. By volume, over 90 percent of total national sulfur oxide emissions are in the form of sulfur dioxide, SO_2. Primary sulfates account for most of the other 10 percent. Little is known about primary sulfates, but combustion of coal and oil is thought to be a major source. Primary sulfates are of increasing concern because of their potential impacts on visibility, acidic deposition, and health.

4.4.2.1 Fuel Combustion--Stationary fuel combustion includes all boilers, heaters, and furnaces found in utilities, industry, and commercial/institutional and residential establishments. In the utility and industrial sectors, coal, and to a lesser degree, oil combustion contribute most of the particulate and sulfur oxides emissions (see Table 4-6). Oil combustion causes most of these emissions from commercial/institutional and residential establishments.

Coal is a slow-burning fuel with a relatively high ash content. Coal combustion particles consist primarily of carbon, silica, alumina, and iron oxide (See Table 4-8). Particulate sulfates and trace elements are also included. A large percentage of the trace elements in raw coal remains in the solid waste or bottom ash, as shown in Table 4-10 (based on 1974 emissions data). The roughly 940,000 metric tons of trace elements emitted to the atmosphere represent about 15 percent of total particulate emissions.

Uncontrolled, the quantity and particle size distribution of coal fly ash depend on the amount and type of coal burned, the unit type, and the ash content of the coal. Cyclone and pulverized-coal furnaces, typically used in utility boilers, discharge finer particles than stoker-fired boilers, used mainly by industry. The combustion of low-ash coal produces less particulate matter than the combustion of high-ash coal. High-sodium lignite causes less combustion particulate formation than does low-sodium lignite (U.S. Environmental Protection Agency, 1977).

TABLE 4-10. TRACE ELEMENT AIR EMISSIONS VS. SOLID WASTE: PERCENT FROM CONVENTIONAL STATIONARY FUEL COMBUSTION SOURCES, AND TOTAL (METRIC TONS PER YEAR)

Element	Air emissions (fly ash)					Solid waste (bottom ash)				
	Util	Indust	Com/Inst	Res	Total	Util	Indust	Com/Inst	Res	Total
As	90	8	2	<1	2,990	89	9	1	1	12,250
Ba	88	9	3	<1	2,770	83	13	2	2	15,970
Be	89	9	2	<1	240	83	12	2	3	740
B	90	9	1	<1	4,990	85	13	1	2	16,240
Br	84	13	2	1	6,080	0	0	0	0	0
Cd	61	21	18	<1	300	83	14	1	2	110
Cl	83	13	2	2	644,100	0	0	0	0	0
Cr	84	11	5	<1	1,630	75	12	5	8	5,040
Co	63	23	14	<1	460	69	9	8	14	1,920
Cu	72	16	12	<1	2,540	78	12	4	6	4,280
F	83	13	2	2	33,570	0	0	0	0	0
Fe	77	20	3	<1	154,200	87	9	2	2	1,369,900
Pb	92	7	1	<1	1,180	81	15	2	3	2,530
Mn	89	10	1	<1	4,630	98	1	1	<1	12,520
Hg	81	14	3	2	50	78	20	2	<1	10
Ni	60	21	19	<1	7,350	81	12	3	4	4,700
Se	85	13	2	1	790	76	22	1	1	370
Ti	89	9	2	<1	56,250	83	13	2	2	178,700
U	86	10	4	<1	1,540	84	13	1	2	4,510
V	63	20	17	<1	9,980	84	12	1	2	8,450
Zn	89	10	1	<1	2,090	83	13	2	3	6,890
Zr	78	20	2	<1	2,090	86	11	1	2	17,240
					939,820					1,662,370

Source: Surprenant et al. (1976).

In the combustion of most coals (most commonly bituminous), more than 90 percent of the coal sulfur is converted to gaseous SO_2; about 1 to 2 percent of the emitted sulfur oxides are in the form of primary sulfates (Homolya and Cheney, 1978a; Homolya and Cheney, 1979).

Lignite is used where it is plentiful at relatively low cost. The alkali content (mostly sodium) of lignite ash has a major effect on the amount of coal sulfur retained in bottom ash. A high-sodium lignite may retain over 50 percent of the available sulfur, and a low-sodium lignite may retain less than 10 percent (U.S. Environmental Protection Agency, 1977).

Several factors can affect the formation of primary sulfates from coal-fired boilers. The higher excess oxygen levels commonly used in industrial boilers increase the oxidation of SO_2 to SO_3 and H_2SO_4 (Homolya and Cheney, 1978a; Bennett and Knapp, 1978). Most gaseous SO_3 is hydrated to gaseous or aerosol H_2SO_4 before exiting the boiler stack (Homolya and Cheney, 1979). Dirty equipment also may increase primary sulfate emissions from coal-fired boilers, since boiler deposits can act as catalysts in the oxidation of SO_2 to sulfates. Conversely, the relatively low flame temperatures used in most coal-fired boilers lessen the formation of SO_3 from SO_2.

After coal, oil combustion in the utility and industrial sectors results in the next largest amount of emissions. In direct contrast to coal, however, oil is a fast burning, low ash fuel. The low ash content results in formation of less particulate matter, but the size of particles formed by oil combustion is generally smaller than that of particles formed by coal combustion (see Table 4-8). Also, although coal combustion contributes most of the trace elements associated with particulate emissions, oil combustion is the source of 50 to 80 percent of cadmium, cobalt, copper, nickel, and vanadium emissions (Surprenant et al., 1976).

Oil-fired boilers generally convert over 90 percent of available fuel sulfur to gaseous SO_2 emissions. However, high flame temperatures used in the combustion of oil exacerbate the formation of primary sulfates. Tests have shown that about 7 percent by weight of sulfur oxide emissions from oil combustion is emitted as primary sulfates (Homolya and Cheney, 1978b). Increasing excess oxygen and increasing the oil vanadium content will increase the formation of primary sulfates in the gas (Homolya and Cheney, 1978b; Bennett and Knapp, 1978; Dietz et al., 1978). As the emissions disperse and cool to ambient temperature, vanadium's catalytic action becomes insignificant (see Chapter 2).

Low sulfur oil and natural gas are the fuels typically used for space heating in the commercial/institutional and residential sectors. Total emissions are minor compared with the utility and industrial sectors. However, most commercial/institutional and residential sources are in areas of high population density and release emissions at or near ground level, thereby providing for high population exposure (Surprenant et al., 1979). Also, emissions are concentrated primarily during the winter heating season.

Currently, homeowners, particularly those in the northern forested areas of the U.S., are turning to wood as a heating fuel. In 1976, a total of 16×10^6 metric tons was combusted in wood stoves and furnaces, auxiliary heating devices, and fireplaces (deAngelis et al., 1980).

The emissions of particulate matter from wood combustion primarily consist of organic matter that is rich in phenols, derivatives of benzaldehyde, and furfural, and a variety of compounds in the general category of polycyclic organic matter (POM). Measurements of the filterable (with collection taking place at 116°C) particles emitted during residential wood combustion typically show levels of approximately 3 g per kg of fuel. Condensable (at 0°C) organic emissions are on the order of 8 g/kg. Of critical importance is the fact that measurements of POM's show values of 0.02 to 0.3 g/kg and 0.03 g/kg for stoves and fireplaces, respectively (deAngelis et al., 1980). On the national scale, exclusive of aircraft emissions, 35 percent of all POM's are emitted from residential wood combustion (Peters, 1981). In 1980, the CO emissions from home wood combustion accounted for about 3 percent of the national total; emissions of sulfur oxides are at least two orders of magnitude less than the particulate emissions. Although emissions from residential wood burning are a small fraction of national totals, they are injected practically at ground level and can be expected to become an increasingly significant component in urban air pollution.

4.4.2.2 Industrial Processes--Major industrial process sources of particulate and sulfur oxide emissions include the metals, mineral products, petroleum, and chemicals industries. Others are grain processing and pulp and paper production (See Table 4-6).

The most significant emission sources in the metals industry are iron and steel and primary smelting operations. The iron and steel industry involves coke, iron, and steel production. Coking is the process of heating coal in a low-oxygen atmosphere to remove volatile components, which are recovered. Coke is used in the production of iron. Both particles and sulfur oxides result from the charging of coal to the hot ovens, door and topside leaks, underfiring, pushing (removal of hot coke), and quenching. Some fine particles consist, at least partly, of condensed organic components.

Particulate emission sources of iron production include the combustion gases, tapping operations, and blast furnace slips (operations that require bypassing the control device). The emitted particles are probably all fine particles that either escape the control device or result from tapping (see Table 4-8). Blast furnace flue dust is composed primarily of iron, silicon dioxide, and aluminum oxide, among others.

Steel is produced in several different ways. The basic oxygen furnace produces steel from a furnace charge composed of about 70 percent molten pig iron and 30 percent scrap. A stream of commercially pure oxygen is used to oxidize impurities, principally carbon and silicon. The tremendous agitation produced by the oxygen lancing produces high dust loadings consisting mostly of iron and small amounts of fluorides. Most of the particles are less than 5 µm in size (U.S. Environmental Protection Agency, 1977).

From 1960 to 1975, steel production in open hearth furnaces declined from 90 percent of the U.S. total to 20 percent (Desy, 1978). Open hearth furnaces are being replaced by basic oxygen furnaces that produce 272 or more metric tons of steel per hour compared with the 27 to 54 metric tons per hour typically produced in open hearth furnaces. The composition of particulate emissions is similar to those from the basic oxygen furnace. Most of the emissions before control are less than 5 µm, and probably 90 percent are fine particles after control.

Two types of electric furnaces, the arc furnace and the induction furnace, are used to produce steel. The arc furnace is used to produce high-alloy steel, as well as a considerable amount of mild steel. The emissions, most of which are fine particles, consist primarily of oxides of iron, manganese, aluminum, calcium, magnesium, and silicon. Particulate fluorides are also emitted. The induction furnace produces primarily specialty and high-alloy steels and has no major emission problems.

The primary metals industry includes the smelting of copper, lead, and zinc, along with aluminum production. Sulfur in unprocessed copper, lead, and zinc ores is converted to SO_2 in the smelting processes (U.S. Environmental Protection Agency, 1977). A relatively small portion of the sulfur is emitted as particulate sulfate and sulfuric acid. The bulk of SO_2 is formed in the roasting, smelting, sintering, and converting processes (U.S. Environmental Protection Agency, 1974). Particulate matter emitted from the same processes is mostly fine particles, less than 2.5 µm in diameter.

Aluminum production involves mainly bauxite grinding, calcining, and reduction. Particulate emissions are primarily alumina with about 25 percent particulate fluoride (U.S. Environmental Protection Agency, 1977). Before control, 35 to 44 percent of the particles were below 1 µm in diameter.

Emissions from the mineral products industry result primarily from the production of Portland cement, asphalt, and crushed rock and to a lesser extent, lime, glass, gypsum, brick, fiberglass, cleaned coal, phosphate rock, and potash. Emission points such as crushing, screening, conveying, grinding, drying or calcining, and loading are common to most mineral products industries. Fugitive dust from most of these processes tends to be larger than 15 µm, although drying and calcining produce relatively finer particles. The composition of particulate emissions is similar to the mineral being processed.

The more than 30 raw materials used to make cement can be grouped into four basic categories: lime (calcareous), silica (siliceous), alumina (argillaceous), and iron (ferriferous). The kiln and associated clinker cooler are potentially the largest sources of particulate and sulfur oxides emissions (U.S. Environmental Protection Agency, 1977). Kiln emissions also include primary sulfates (Dellinger et al., 1980). Probable particle size distribution and chemical composition are shown in Table 4-8.

Asphalt concrete is a mixture of aggregate, asphalt cement, and occasionally mineral filler. Commonly, asphalt concrete is produced in conjunction with crushed and broken stone production facilities. The rotary dryer typically used to dry and heat the aggregate is potentially the largest particulate emission source (U.S. Environmental Protection Agency, 1977).

Emissions from the production of crushed rock result primarily from the processes mentioned earlier. The chemical composition of particulate emissions is similar to the material processed. Usually, the particles emitted are relatively coarse.

The major sources of sulfur oxide emissions in the petroleum industry are the catalytic cracking and sulfur recovery processes and off-gas flares (U.S. Environmental Protection Agency, 1977); Dickerman et al., 1977). Sulfur dioxide is emitted during the catalyst regeneration step of the catalytic cracking process.

Major sour gas streams are usually treated in a sulfur plant. Most sulfur plants utilize a modified Claus process that consists of multistage oxidation of hydrogen sulfide to elemental sulfur. The sulfur recovery efficiency of these sulfur plants ranges from 92 to 97 percent depending on the number of catalytic stages. Sulfur plant tail gas is usually incinerated so that most of the remaining sulfur species are oxidized to SO_2. Some plants have installed tail gas cleanup systems to reduce SO_2 emissions further. These units along with a sulfur plant can achieve up to 99.8 percent sulfur recovery.

Minor off-gas streams and recovered vapors are often combusted in flares. Most of the sulfur species present in these vapors are oxidized to SO_2.

A variety of processes are used by the chemical production industry. Chemical process industries that contribute significant amounts of sulfur oxide emissions are sulfuric acid plants, elemental sulfur plants, and explosives manufacturing.

Sulfuric acid is manufactured primarily by the contact process. The three types of raw materials charged to sulfuric acid plants are elemental sulfur, spent acid and hydrogen sulfide, and sulfide ores and smelter gases. The amount of SO_2 emissions in acid plant exit gases is an inverse function of the sulfur conversion efficiency of the process (U.S. Environmental Protection Agency, 1977). Sulfuric acid mist is generated by the process SO_2 absorbers. The quantity and size distribution of the acid mist are dependent on the type of sulfur feedstock used, the strength of the acid produced, and the conditions in the absorber.

The manufacture of TNT and nitrocellulose explosives produces emissions of SO_2 and sulfuric acid mist. Sulfuric acid is a major raw material in the production of these explosives. Sulfuric acid concentrators, exhaust from the preparation of sodium sulfite/sodium hydrogen sulfite (Sellite), and incinerators are the major sulfur oxides sources in these processes. Sulfur oxide emissions may vary considerably depending on the efficiency of the process and the operating conditions (U.S. Environmental Protection Agency, 1977).

Particulate emissions from grain processing typically result from handling, cleaning, drying, and milling (U.S. Environmental Protection Agency, 1977). Grain processing particles are normally coarse and composed of the parent organic material.

Chemical wood pulping by the kraft or sulfite processes involves cooking wood chips under pressure to dissolve the lignin that binds the cellulose fibers, in addition to washing, milling, bleaching, and drying (U.S. Environmental Protection Agency, 1977). Particulate emissions occur primarily from the recovery furnace (used to recover cooking chemicals) and the lime kiln (lime is used in cooking). Sulfur dioxide emissions result mainly from oxidation of reduced sulfur compounds in the recovery furnace.

4.4.3 Industrial Process Fugitive Particulate Emissions

Fugitive dust emissions result from wind erosion of storage piles and unpaved plant roads and from vehicular traffic over plant roads. Fugitive process emissions result from industry-related operations such as materials handling, loading, unloading, and transfer operations. Point sources that are incompletely controlled, such as furnace charging and tapping, and equipment that is maintained poorly, such as leaking furnaces and coke oven doors, are also fugitive process emission sources.

Process fugitive emissions are not emitted from a definable point such as a stack. They are difficult to collect, measure, and control. A given industry generally has a large number of fugitive particulate emission sources. For example, 20 separate sources have been identified for foundries (Jutze et al., 1977). In terms of total emissions, however, one or two of these sources may predominate.

Even though fugitive particulate emission totals may appear small when compared with totals from large point sources, they may take on importance because of the concentration of control efforts on point source emissions. In the integrated iron and steel industry, where fugitive particulate emissions are characterized relatively well, fugitive emissions are estimated to account for about 10 percent of all uncontrolled emissions. However, since fugitive particulate emissions are poorly controlled, they account for more than 60 percent of total controlled emissions (Spawn, 1979). Also, in situations where point sources are well controlled or use high stacks, fugitive particulate emissions exert a major effect on local air quality. Extremely high suspended particulate matter levels have been measured in areas where process fugitive emissions are predominant (Lynn et al., 1976; Lebowitz, 1975).

Table 4-11 presents estimates of uncontrolled industrial process fugitive particulate emissions. Particle size and composition characteristics are also presented. Unfortunately, many of the emission factors used to estimate process fugitive emissions are based on engineering judgment or extrapolation from similar processes. Often, few test data are available to support these estimates since process fugitive emissions are difficult to measure. Therefore, the accuracy of these estimates is questionable. Also, some of the emissions presented in Table 4-11 may have already been accounted for in Table 4-6 (Section 4.4.2). This overlap results from the use of different references (see Section 4.3).

As is evident from Table 4-11, three broad categories account for nearly all of the potential process fugitive emissions in the United States. They are mineral products, food and agriculture, and primary metals. In the mineral products industries, fugitive particulate emissions tend to reflect the composition of the parent materials. The limited amount of particle size data indicates that most particles are relatively coarse.

Grain elevator operations account for the fugitive particulate emissions in the food and agriculture industry. These emissions consist almost entirely of grain dust from loading and

TABLE 4-11. UNCONTROLLED INDUSTRIAL PROCESS FUGITIVE PARTICULATE EMISSIONS[a]

Source category	Annual uncontrolled fugitive particulate emissions (10^3 metric tons)	Size characteristics	Major components
Mineral products			
Crushed rock			
Extraction,			
Surface coal mining	730	10-50% < 10 μm 1-2% < 1 μm	Same as parent material (important for toxic minerals such as asbestos, beryllium, silica)
Portland cement	700	10-15% < 10 μm	Limestone, clay, shale, gypsum, iron-bearing and siliceous materials
Asphalt concrete	100	50-70% < 4 μm	Sand, crushed stone, limestone, hydrated lime
Lime manufacturing	50	45-70% < 5 μm	Limestone, lime
Concrete batching	30	10-20% < 5 μm	Cement dust
Food and agriculture			
Grain elevators	1,250	40% < 10 μm	Grain dust
Primary metals			
Coke/iron/steel	250	Coke mfg: 27-80% < 10 μm, 15-26% < 2 μm; iron mfg: 1-10% < 5 μm; Steel mfg: 50% < 5 μm	Polycyclic organic matter, coal dust, coke dust, iron oxide dust, kish (graphite material), metal fume (primarily iron oxide), plus trace amounts of As, Be, Pb, Cr, Cd, Se, Co, Ni, and fluorides
Foundries	125	50% < 15 μm	Metal oxide fume (primarily oxides of silicon and iron), fine carbonaceous fume, plus trace amounts of Pb, Cr, Ag, Co, and Ni

TABLE 4-11. (continued)

Source category	Annual uncontrolled Fugitive particulate emissions (10^3 metric tons)	Size characteristics	Major components
Aluminum	60	50-90% < 10 μm	Particulate fluorides, alumina (Al_2O_3), carbon dust, condensed hydrocarbons, tars
Copper	40	10-50% < 5 μm	Cu, Fe, S, SiO_2 from ore concentrate; metal fume consisting of oxides of As, Pb, Zn, Cu, Cd, plus trace amounts of Se and Ag
Lead	15	10-90% < 5 μm	Metal fume consisting of oxides of Pb, Cd, Zn, Sb, plus trace amounts of As, Se, and Ag
Secondary metals	10	80-100% < 5 μm	Oxides of Al,Cu,Pb, Sn,Zn; oxides of alkali metals; $AlCl_3$, NH_4Cl,NaCl, $ZnCl_2$; fluorides, and carbonaceous materials, plus trace amounts of Cr, Cd, and Ni
Wood products	10	40-90% < 10 μm	Sawdust
TOTAL	3,370		

Note: Emissions are based on data for the mid-1970's and may differ from current levels.

[a]Sources: Taback et al. (1979)
Zoller et al. (1978)
Jutze et al. (1977)
Norman et al. (1977)

unloading, drying and cleaning operations, conveyor belts, and transfer points. Only about 29 percent of these particles are less than 10 μm in size.

Primary metals production encompasses six separate industries. Fugitive particulate emissions in this category result from the handling and transporting of raw materials and from the smelting and refining of these raw materials into their finished metal products. Although emissions of the first type are not well characterized, emissions of the second type often consist of fine metal fumes. This finding is particularly significant because of the quantities of toxic trace metals that can be concentrated and volatilized in metal melting operations. Some of these trace toxic components of particulate emissions are identified in Table 4-11.

The remaining two categories, secondary metals and wood products, account for less than 1 percent of the national total of industrial process fugitive particulate emissions. Fugitive metal fume particles from secondary metal melting operations also include toxic components and are listed in Table 4-11.

4.4.4 Nonindustrial Fugitive Particulate Emissions

Nonindustrial fugitive particulate emissions, or fugitive dusts are caused by traffic entrainment of dust from public paved and unpaved roads, agricultural operations, construction activities, surface mining operations, and fires. With the exception of fires, all of these sources may be classified as open-dust sources; that is, they involve dust entrainment by the interaction of machinery with aggregate materials and by the forces of wind on exposed materials.

A number of factors can affect emissions from open sources but they can generally be classified under three headings: material, equipment, and climate. Material factors encompass such influences as silt and moisture content. For example, increasing the silt content and decreasing the moisture content of unpaved road material would probably result in more dust being generated. Equipment factors generally refer to vehicle weight and speed. For example, increasing the speed or weight of a vehicle travelling over an unpaved road would tend to increase emissions. Climatic factors are windspeed and precipitation. Increased windspeed and decreased precipitation would both tend to increase emissions from any open-dust source.

Estimated U.S. annual particulate emissions from nonindustrial fugitive dust sources are difficult to estimate accurately. As shown in Table 4-12, fugitive dust emissions from unpaved roads tend to be quite significant. The two available estimates, however, vary by almost an order of magnitude. Fugitive dust from wind erosion of cropland and construction activities as documented by Cooper et al. (1979) also appears significant. However, no other estimates are available for comparison purposes. Estimated total fugitive emissions range from approximately 112 x 10^6 metric tons per year to 369 x 10^6 metric tons per year. The lower figure assumes the U.S. Environmental Protection Agency (1980b) estimate of fugitive emissions from paved and unpaved roads; the higher figure assumes the estimate of Cooper et

TABLE 4-12. ESTIMATED ANNUAL PARTICULATE EMISSIONS FROM NONINDUSTRIAL FUGITIVE SOURCES

Source category	Estimated Emissions (10^6 metric tons/year)[a] Cooper et al. (1979)	U.S. Environmental Protection Agency (1980b)
Unpaved roads	290	35
Paved roads	7.2	4.7
Wind erosion of cropland	40	-
Agricultural tilling	2.9	-
Construction activities	25	-
Minerals extraction	3	-
Mineral tailing	0.7	-
Prescribed fires[b]	0.4	0.2

[a] Particles less than 30 μm in diameter.

[b] Includes prescribed forest burns and agricultural burning.

TABLE 4-13. ESTIMATED PARTICLE SIZE DISTRIBUTIONS FOR SEVERAL NONINDUSTRIAL FUGITIVE SOURCE CATEGORIES IN CALIFORNIA'S SOUTH COAST AIR BASIN

Source category	Weight percent in size range >10 μm	3-10 μm	1-3 μm	<1 μm
Unpaved road dust	54	16	12	18
Agricultural tillage dust	40	21	17	22
Road building and construction dust	36	24	16	24
Agricultural burning	<1	2	8	90

Source: Taback et al. (1979).

al. (1979). Because of the disparity between comparable estimates, the estimated emissions presented in Table 4-12 should be considered with a degree of caution.

Information on particle size distribution is also limited. Some limited data are presented in Table 4-13, but they are representative only of California's South Coast Air Basin and should not be extrapolated to the Nation as a whole. Dust from unpaved roads, agricultural tilling, construction, and road building is composed primarily of silicon, phosphorus, aluminum, iron, calcium, and potassium. Trace elements include barium, cobalt, copper, lead, manganese, nickel, titanium, vanadium, and zinc (Taback et al., 1979)

Finally, it is estimated that fugitive dust emissions exceed particulate emissions from stationary point sources in 90 percent of the Air Quality Control Regions that are not meeting the ambient standards for total suspended particulates (Carpenter and Weant, 1978). However, the impact of fugitive dust emissions on populated areas may be somewhat lessened because a major portion of these emissions consists of large particles that settle to the ground a short distance from the source and because many fugitive dust sources, like unpaved roads, exist mainly in rural areas (U.S. Environmental Protection Agency, 1980b).

4.4.5 Transportation Source Emissions

Transportation source emissions may be divided into two categories: engine-related emissions from vehicle exhaust, and other highway vehicle-related particles from tire wear and clutch and brake lining wear (Bradow et al., 1979; U.S. Environmental Protection Agency, 1978b; Dannis, 1974; and Jacko and DuCharme, 1973). Total transportation source emissions for 1978, including emissions from highway vehicles, aircraft, railroads, and vessels, were estimated at 1.3 x 10^6 metric tons (particulate matter) and 0.8 x 10^6 metric tons (sulfur oxides) (U.S. Environmental Protection Agency, 1980a). About 75 percent of the particulate emissions and 50 percent of the sulfur oxide emissions in 1978 were from highway vehicles.

Engine-related particulate emissions from transportation sources are composed primarily of lead halides, sulfates, and carbonaceous matter (including absorbed organics). Highway vehicle-related particles are emitted at the rate of about 0.01 to 0.30 grams per mile by gasoline engines and 0.5 to 3.0 grams per mile for diesel engines (Bradow et al., 1979). The major components are lead (except for vehicles using diesel fuel or unleaded gasoline), carbon, organics, and sulfates. Vehicles burning leaded gasoline also emit inorganic compounds of lead (mostly PbBrCl), bromine, and chlorine (Springer, 1978). Particulate matter from catalyst-equipped vehicles using unleaded gasoline is dominated by sulfate and carbonaceous material.

Diesel exhaust particles can include traces of iron, copper, calcium, lead, and zinc, along with carbon, organics, and sulfates (Lee and Duffield, 1979). The particle emission rate and composition for diesel engines are sensitive to many factors, including vehicle size, operating conditions (speed, load), and fuel characteristics. Normally, carbon-containing species dominate, including a material similar to lubricating oil (Black and High, 1978).

Engine-related particles are mostly under 1 μm in diameter. For vehicles burning leaded gasoline, the available data indicate a mass median diameter of about 0.25 μm (Moran et al., 1971). Due to the predominance of sulfates, catalyst-equipped vehicles burning unleaded gasoline emit smaller particles having a mass mean diameter of about 0.05 μm (Groblicki, 1976). The size distribution of diesel particulate matter suggests a mass median diameter of about 0.2 μm (Dolan and Kittelson, 1979).

Very few data exist on nonengine particulate emissions from highway vehicles. About 40 percent of particles from tire wear are less than 10 μm (about 20 percent are less than 1 μm); they are composed primarily of carbon (Taback et al., 1979). Particles from brake lining attrition are all less than 1 μm and are composed mainly of asbestos (80 percent) and carbon (Taback et al., 1979).

4.5 SUMMARY

Particulate matter and sulfur oxides are emitted into the atmosphere from a number of sources, both natural and manmade. Natural source emissions include terrestrial dust, sea spray, biogenic emanations, volcanic emissions, and emissions from wildfires. The predominant manmade sources are stationary point sources, industrial and nonindustrial fugitive sources, and transportation sources. Annual U.S. emissions from natural sources are estimated at 84 x 10^6 metric tons of particulate matter and 5 x 10^6 metric tons of sulfur (the equivalent of 10 x 10^6 metric tons of sulfur dioxide). Manmade sources emit roughly 125 to 385 x 10^6 metric tons of particulate matter per year and 27 x 10^6 metric tons of sulfur oxides per year in the U.S. Because of the assumptions and approximations inherent in emissions calculations, the numbers quoted above should not be considered more than estimates. Section 4.2 further discusses the problem involved with emissions estimates.

The characteristics of particulate matter emissions vary according to source type and a number of other factors. Particulate emissions from natural sources tend to be rather coarse. (For the purposes of this chapter, coarse refers to particles with a diameter greater than 2.5 μm.) Particulate matter generated by nonindustrial fugitive sources (e.g., unpaved roads and wind erosion of cropland) is quite significant on a mass basis. However, only about 50 and 20 percent is less than 10 and 1 μm, respectively. Most of the particulate matter emitted by stationary sources and transportation sources, on the other hand, is relatively fine, or less than 2.5 μm in diameter. Adding control devices further concentrates particulate emissions in the finer ranges because most control devices are more efficient at removing larger particles. Therefore, the estimated 10.5 x 10^6 metric tons of particulate matter generated in 1978 by stationary point sources probably consists largely of finer particles, since that estimate was arrived at assuming the application of control devices. In addition, the finer particles emitted by stationary point sources tend to include a greater variety of toxic substances than do emissions from natural or manmade fugitive sources.

Virtually all of the manmade sulfur oxide emissions result from stationary point sources. Over 90 percent of these manmade sulfur oxide emissions are in the form of sulfur dioxide.

The balance consists of sulfates in various forms. Most natural sulfur is emitted as reduced sulfur compounds, but these compounds are probably oxidized in the atmosphere to sulfur dioxide and sulfates.

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5. ENVIRONMENTAL CONCENTRATIONS AND EXPOSURE

5.1 INTRODUCTION

This chapter has two objectives: (1) to delineate the concentrations of SO_2 and particles suspended in the air to which human populations, other organisms, and manmade objects are exposed; and (2) to show how various sources of air pollutants contribute to these exposures.

The first goal is to describe ambient air concentrations of these two pollutants in a way which is relevant to the effects they might cause. Measurements of SO_2, TSP, and some chemical components of PM in the ambient air have been made for a long time, mostly with imperfect methods and procedures. In Chapter 3, the most current information relative to sources of error in measurement are covered in detail. Here, only those issues that influence interpretation are mentioned and then only briefly. The reader is advised to consult Chapter 3 for more detail.

Despite imperfections in measurement methods, State and local monitoring data stored by EPA are the largest available source of information on long-term trends in pollutant concentrations and on the geographical distributions of the pollutant levels. Therefore, the existing monitoring data are presented first to provide an overall perspective regarding SO_2 and PM concentrations encountered in the ambient air.

Particulate matter, as a pollutant class, is exceedingly complex both in regard to its physical properties and its chemical composition. In Chapter 2, those characteristics of particles generally observed in most atmospheres are discussed in detail. Consequently, in this section only those features of chemical composition and physical size are treated that influence data interpretation. The reader is directed to Chapter 2 for more detail on these subjects.

Recently, particle measurements have been collected and analyzed to estimate the relative contributions of important sources. In this case, the elemental and chemical complexity of the particles proves to be valuable since many source types have identifiable characteristic chemical signatures. Consequently, it is often possible to make at least approximate assignments of the relative amounts of suspended PM derived from road dust, power plants, automobiles, and other common sources, provided that an adequate description of the source signature is available. Since this technique is still new, only a few studies are available, some of which are discussed to show the approximate source contributions in representative cases. For a more complete description of particle emission factors and inventories, Chapter 4 should be consulted.

Ultimately, the importance of the ambient air measurements of pollutant concentrations is in identifying and predicting undesirable effects. When the effect considered is visibility reduction, the important factors are concentrations of light scattering and absorbing particles over the geographical scale of several miles. In materials damage, concentrations of SO_2 and of soiling particles are important over time scales of months or years. When considering effects other than visibility, the important matter is the dose. Dose incorporates concentration, time, uptake and loss, and the relationship among these parameters. Throughout their lifetime, people inhale a complex mixture of gases and particles. Other living things, vegetation and animals, are also exposed to the same complex mixtures, the composition of which varies with time at any given location because of changing atmospheric conditions and source contributions. The biological effects of air pollution are functions of dose delivered to the receptor and the ability of the receptor to cope with the resultant stress. In humans, the stress experienced by a critical organ or receptor tissue from particle inhalation depends on particle size, composition, morphology, acidity or alkalinity, and other physicochemical properties of the aerosol. The delivered dose is also a function of the anatomical features of the receptor as well as the manner of breathing, breathing rate, and integrity of bodily defense systems.

It is almost impossible to measure directly the air pollution dose to a population or even to an individual, except in the laboratory. As an alternative to direct measurement of dose, exposure can and often must be used as an approximation of dose for studies on air pollution risk and effects. The exposure-response relationship for air pollution is most important for establishing standards. Unfortunately, to extrapolate from measurements of ambient levels at a few locations to individual or population exposure levels is a very difficult task at present. The contribution of outdoor air to indoor concentrations is still being investigated. The additional exposures to gases and particles from nonoccupational indoor sources are not adequately known.

Indoor air quality and activity patterns complicate air pollution exposure estimates and are discussed later in this chapter. First, the ambient outdoor concentrations of SO_2 and PM are examined.

5.2 AMBIENT MEASUREMENTS OF SULFUR DIOXIDE

Ambient concentrations of SO_2 are determined by the following factors:

1. Density of emission sources.
2. Source characteristics such as stack height, exit velocity, and source strength.
3. Local meteorological conditions.
4. Local topography and surrounding buildings.
5. Reaction rate for oxidation of SO_2.
6. Removal rates by precipitation, deposition at surfaces, and other reactions.

These factors interact in such a way that in urban and industrialized areas with high densities of SO_2 emissions, the SO_2 concentrations are much higher than in surrounding rural areas. It is quite common to find gradients in SO_2 concentration within these industrialized areas, with a central core area reporting the highest SO_2 concentrations. This pattern is shown diagrammatically in Figure 5-1.

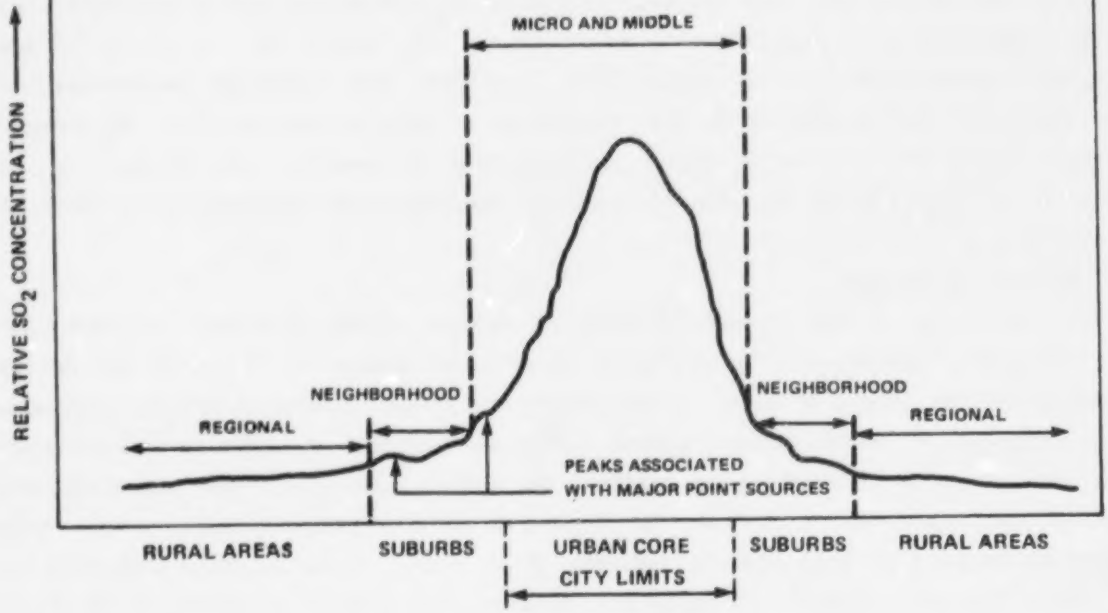
RELATIVE SO2 CONCENTRATION
MICRO AND MIDDLE
NEIGHBORHOOD
REGIONAL
NEIGHBORHOOD
REGIONAL
PEAKS ASSOCIATED WITH MAJOR POINT SOURCES
RURAL AREAS
SUBURBS
URBAN CORE
CITY LIMITS
SUBURBS
RURAL AREAS

Figure 5-1. Distribution of annual mean sulfur dioxide concentrations across an urban complex, as a function of various spatial scales.

Source: Ball and Anderson (1977).

Where SO_2 emissions are dominated by a single source or a few point sources, the pattern of SO_2 concentrations could be different from the pattern displayed in Figure 5-1. Depending on topography, meteorology, and source characteristics, the concentration patterns may be asymmetrical, and the temporal distribution may be skewed to low mean values with a few intermittent high peaks. These differences in concentration patterns may be important in relation to the types of effects experienced in exposed human populations.

Most urban areas have experienced dramatic improvements in air quality as a result of restrictions on sulfur in fuel, better controls on new and existing sources, displacement of old sources and building of new sources in less populated regions, and construction of taller stacks.

This section presents SO_2 concentration data for specific locations and areas where levels are currently high. The national status of SO_2 concentrations is reviewed, along with temporal trend data. A comparison is made between SO_2 levels in six cities in the early 1960's and concentrations in the late 1970's. Insights into important determinants of population exposures are presented in the discussion of diurnal and seasonal SO_2 concentration patterns. Since SO_2 can be measured by a variety of methods (see Chapter 3), a brief discussion of SO_2 monitoring and instruments precedes the substantive sections on concentrations.

5.2.1 Monitoring Factors

The EPA is now in the process of revising Federal, State, and local air monitoring networks. By 1981, States will be operating a selected number of sites in the National Air Monitoring Station (NAMS) Network. These sites are to be located in densely populated areas with the highest pollutant concentrations. They are designed to serve in assessing pollutant trends and progress in meeting standards. By 1983, State and local agencies are to be operating the State and Local Air Monitoring Station (SLAMS) Network. This network is designed to be part of each State's implementation plan. It is expected that this will mean fewer sites than are currently in operation; however, the Federal coordination of air monitoring should provide much-needed quality control. The trend toward reduction in the number of stations is already apparent in the 1977 SO_2 data. There were 117 fewer monitoring sites reporting data in 1977 than in 1976 (2365 versus 2482). Many States terminated all or most of their 24-hour West-Gaeke bubbler sampling in 1978, and most remaining bubbler stations are being fitted with temperature controls to avoid sample degradation (see Chapter 3). However, state and local agencies are relying primarily on continuous monitoring equipment whenever possible.

Nationally, SO_2 monitoring is not as extensive as TSP monitoring. In 1978 there were 947 sites with continuous monitoring equipment and 1298 bubbler sites. Every State conducted SO_2 monitoring. All reported sites produced useful information on short-term (1- to 24-hour) SO_2 concentrations. However, only those sites reporting a specified number of hourly or daily observations per year are considered valid in terms of their annual mean. For the EPA, minimum criteria for a valid annual mean are 6570 hourly values from a continuous monitor or five 24-hour values in each quarter from a bubbler monitor. It is in the number of SO_2 sites with valid annual means that national coverage appears inadequate. Only 99 of the 1298 bubbler sites (or 7.6 percent) had valid annual means in 1978; only 385 of the 947 (or 40.7 percent) continuous sites were considered valid. There were seven States with no valid annual SO_2 data for 1978. The EPA is currently taking steps to improve the quality of SO_2 data and to increase the number of representative sites reporting valid data.

For valid bubbler sites, the average number of 24-hour observations in 1978 was 60. The number of observations per site ranged from 28 to 322. For the valid continuous sites, the mean number of observations was 7806 hourly measurements. This ranged from a minimum of 6578 hours to a maximum of 8755 hours.

5.2.2 Sulfur Dioxide Concentrations

Although there are natural sources of SO_2 such as volcanoes (see Chapter 4) that can be important in proximity to the source, they are usually unimportant on an urban scale. Sulfur dioxide has a rather short half-life in the troposphere (see Chapter 6), and background levels are often below the monitor's detection limit. Therefore, it is not surprising that the reported annual mean SO_2 concentration is 3 $\mu g/m^3$ in some nonurban locations. It may be lower; most monitoring techniques have detection limits close to 10 $\mu g/m^3$, and apparent zero values are commonly recorded as half the detection limit.

Monitoring in urbanized areas near industrial sources that use sulfur-bearing fuels shows rather high concentrations of SO_2. In 1978 the annual mean concentrations obtained by SO_2 bubblers ranged from 3 to 79 $\mu g/m^3$. The valid continuous monitors registered 1978 annual mean concentrations ranging from 3 to 152 $\mu g/m^3$.

The concentration of SO_2 is affected by meteorological variables influencing transport, dispersion, and removal, as well as by topography and configuration of sources. Spatial and temporal variations in these parameters are reflected in the range of maximum and 90th percentile concentrations reported across the Nation. For bubbler sites, the lowest 24-hour maximum value reported by a site was 3 $\mu g/m^3$; the highest was 907 $\mu g/m^3$. For the valid continuous sites, the spread of 24-hour maximum values was greater, ranging from 10 $\mu g/m^3$ at one site to 2512 $\mu g/m^3$ at another site. Among all continuous sites reporting in 1978, the extreme 24-hour value was 3931 $\mu g/m^3$.

Figure 5-2 presents the distribution of annual averages for all valid continuous monitoring sites in 1978. On this time scale, the most commonly measured values fell between 20 and 30 $\mu g/m^3$, with most values below 60 $\mu g/m^3$. Most monitoring stations were situated specifically to detect higher urban or source-specific levels of SO_2, however, and the data in Figure 5-2 may be judged more nearly representative of populated areas or areas influenced by specific sources rather than the entire U.S. land area. The following section discusses the effect of site location.

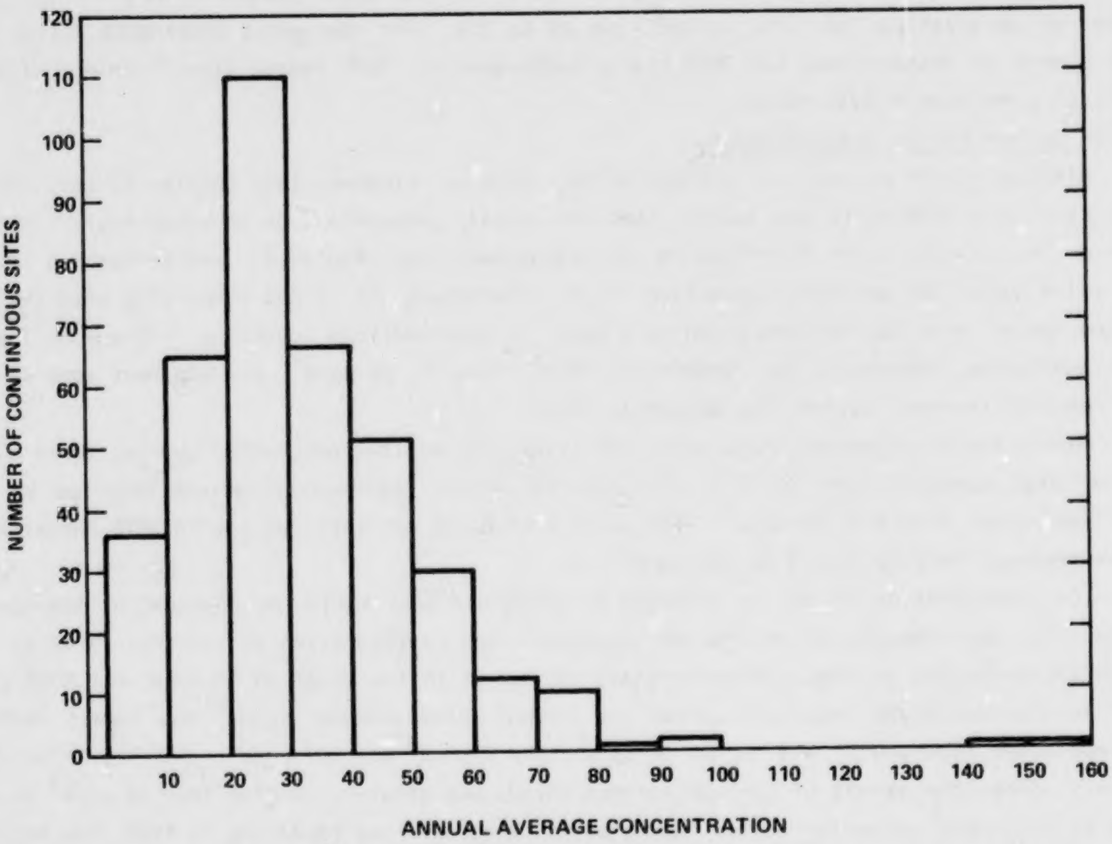

Figure 5-2. Histogram delineating annual average sulfur dioxide concentrations for valid continuous sampling sites in the United States in 1978.

Source: SAROAD.

5.2.3 Sulfur Dioxide Concentration By Site and Region

5.2.3.1 Analyses by Various Site Classifications--In this section, the distributions of annual mean and 90th percentile SO_2 concentrations by site descriptors are presented for bubbler and for continuous sampling methods. A two-descriptor code has been assigned to each site. Distributions for every combination of Type 1 (population, source, background) and for Type 2 (central-city, suburban, rural, remote) are not presented. In some cases the designations are contradictory, such as "population-remote" or "background-central city." The purpose of presenting these distributions is to permit comparison of these two categories of sampling methods and to examine the SO_2 concentrations as a function of location.

In Table 5-1, a cross-tabulation of mean concentrations by method is presented for center-city sites that are primarily either population oriented or source oriented. The third and fourth numbers in each cell are the column percentage and total percentage of sites having concentrations within the designated range. Examination of each of these numbers reveals that bubblers are, on the average, reporting lower concentrations than the continuous instruments, an expected result because of the method biases reported in Chapter 3. In Table 5-1, 14.4 percent of the population-oriented continuous monitors reported mean concentrations above 62 $\mu g/m^3$, whereas only 1.6 percent of the bubblers reported such concentrations. Of the source-oriented sites, a higher percentage (7.1 percent) of the bubblers were above 62 $\mu g/m^3$, but this was still less than the 12.5 percent of the continuous monitors in this category.

5.2.3.2 Regional Comparisons--Regional differences in SO_2 concentrations are not striking. In part, this is the result of the location of the monitor. In Section 5.2.4, it is shown that high SO_2 levels are found around smelters in otherwise clean areas. In the eastern and northern States, most continuous SO_2 monitoring is in urbanized areas In 1978, mean concentrations across all continuous monitors in Regions I, II, III, IV, and V ranged from 23 $\mu g/m^3$ to 51 $\mu g/m^3$ (see Table 5-2). The maximum annual mean among the valid sites in these regions ranged from 59 $\mu g/m^3$ in Region I to 140 $\mu g/m^3$ in Region III. In the less industrialized or less populated regions (VI through X), the mean annual concentration across all sites in each region ranged from 8 $\mu g/m^3$ to 40 $\mu g/m^3$.

Even with the summary of the 1978 continuous SO_2 data, it is difficult to speculate on regional differences in SO_2 concentrations. Sulfur dioxide monitors are not systematically sited for population exposure monitoring purposes; sometimes SO_2 instruments are used for monitoring the local influence of strong point sources (e.g., the smelters noted above). Therefore, better indicators of regional differences in SO_2 concentrations and population exposures are sulfur emission patterns (see Chapter 4).

The data base used in compiling Figure 5-3, collected between 1974 and 1976, offers finer spatial resolution of national SO_2 concentrations on a county scale. The second highest 24-hour average SO_2 concentration by county is displayed. Some areas in the West with extremely high concentrations were still problem areas in the late 1970's (see Table 5-3). Several counties and cities are still reporting high concentrations; however, one should not infer that the reported concentration prevails throughout the county. High readings may exist at

TABLE 5-1. CROSSTABULATION OF ANNUAL MEAN SO_2 CONCENTRATION BY METHOD (BUBBLER OR CONTINUOUS) FOR POPULATION-ORIENTED AND FOR SOURCE-ORIENTED CENTER-CITY SITES

Annual mean SO_2 concentration, $\mu g/m^3$	Purpose of Site					
	Population			Source		
	Bubbler	Continuous	Row Total	Bubbler	Continuous	Row Total
2-7						
Number of sites	139	15	154	9	3	12
Percent of row	90.3	9.7	--	75.0	25.0	--
Percent of column	27.6	5.3	--	16.1	6.3	--
Percent of total	17.7	1.9	19.6	8.7	2.9	11.5
7-18						
Number of sites	159	32	191	18	10	28
Percent of row	83.2	16.8	--	64.3	35.7	--
Percent of column	31.6	11.3	--	32.1	20.8	--
Percent of total	20.2	4.1	24.3	17.3	9.6	26.9
18-33						
Number of sites	106	86	192	12	14	26
Percent of row	55.2	44.8	--	46.2	53.8	--
Percent of column	21.1	30.3	--	21.4	29.2	--
Percent of total	13.5	10.9	24.4	11.5	13.5	25.0
33-62						
Number of sites	91	110	201	13	15	28
Percent of row	45.3	54.7	--	46.4	53.6	--
Percent of column	18.1	38.7	--	23.2	31.3	--
Percent of total	11.6	14.0	25.5	12.5	14.4	26.9
>62						
Number of sites	8	41	49	4	6	10
Percent of row	16.3	83.7	--	40.0	60.0	--
Percent of column	1.6	14.4	--	7.1	12.5	--
Percent of total	1.0	5.2	6.2	3.8	5.8	9.6
Column total						
Number of sites	503	284	787	56	48	104
Percent of total	63.9	36.1	100.0	53.8	46.2	100.0

Note: 1 ppm SO_2 = 2620 ug/m^3.

Source: SAROAD.

TABLE 5-2. CONTINUOUS SO_2 MONITOR RESULTS BY REGION, $\mu g/m^3$

Region	Type	Number of sites	Number of observations per site				Arithmetic Means				90th Percentile			
			Min.	Mean	Max.	s.d.	Min.	Mean	Max.	s.d.	Min.	Mean	Max.	s.d.
I	Valid	22	6665	7519	8416	567	16	33	59	12	34	65	147	27
	All	72	185	4582	8416	2720	8	39	138	23	14	77	340	52
II	Valid	51	6597	7540	8697	546	15	37	78	16	35	72	159	30
	All	87	140	5815	8697	2380	15	41	94	19	35	78	173	33
III	Valid	26	6578	7562	8638	670	12	51	140	23	34	97	282	46
	All	108	94	4381	8638	2534	7	45	140	21	14	86	282	40
IV	Valid	100	6678	8305	8755	574	5	23	63	12	9	54	135	27
	All	203	421	5754	8755	2848	3	23	77	13	3	49	180	29
V	Valid	111	6580	7640	8715	625	7	36	84	16	10	70	167	30
	All	254	129	5512	8715	2327	3	37	192	25	5	73	501	50
VI	Valid	13	6631	7443	8452	607	3	13	31	7	3	31	69	19
	All	32	1669	5461	8452	2072	3	12	56	13	3	29	160	38
VII	Valid	13	6769	7540	8325	439	6	31	47	14	13	62	94	25
	All	38	334	4676	8325	2624	4	25	82	20	5	52	155	41
VIII	Valid	12	6741	7739	8624	514	3	40	152	47	3	100	488	146
	All	49	373	4694	8624	2358	3	34	152	39	3	89	488	113
IX	Valid	19	6857	7952	8638	507	3	8	29	6	3	16	48	12
	All	52	105	4973	8638	2525	3	24	87	20	3	49	213	49
X	Valid	18	6651	7854	8677	464	13	34	78	18	35	90	150	38
	All	29	625	6158	8677	2526	13	33	78	17	29	72	150	38

Note: 1 ppm SO_2 = 2620 ug/m^3.

Source: SAROAD.

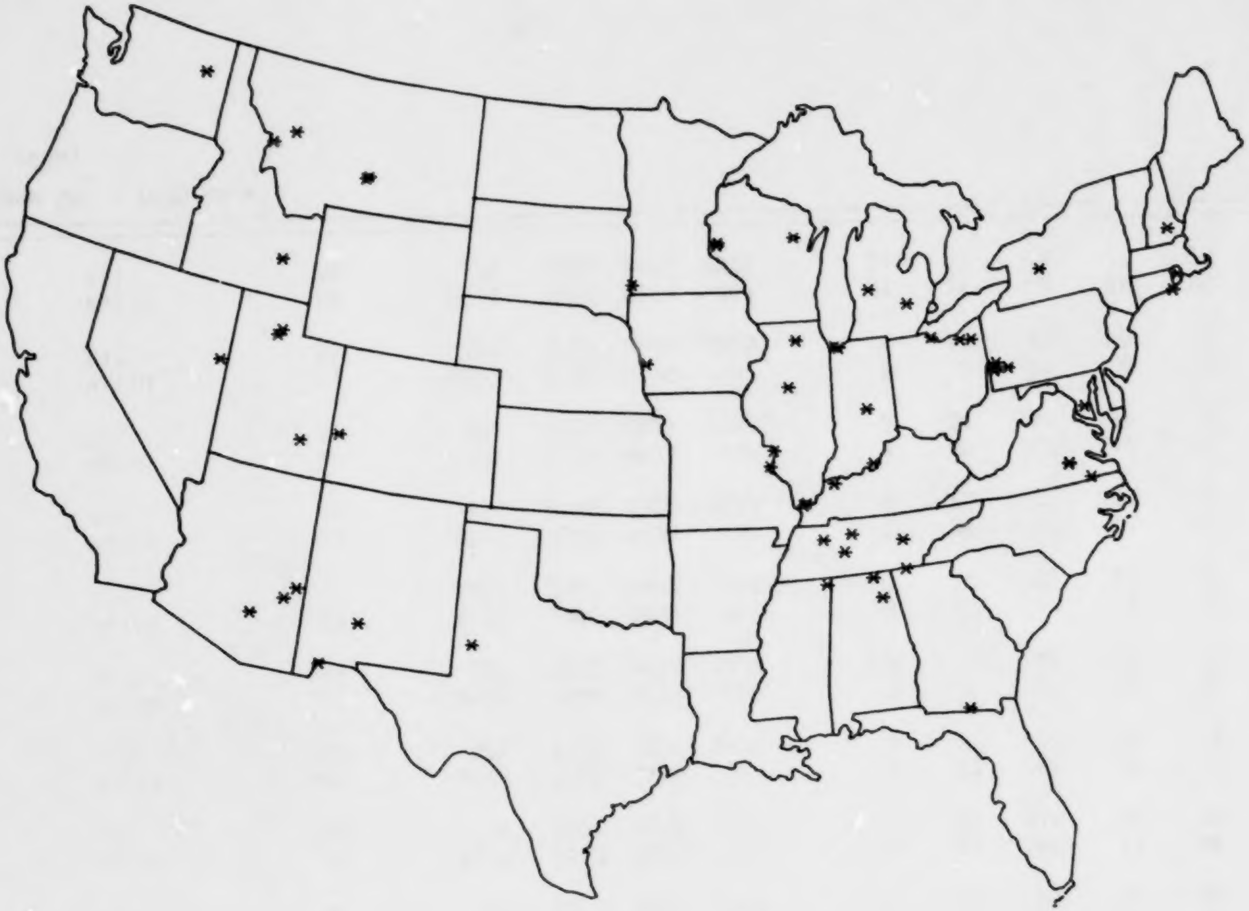

Figure 5-3. Characterization of 1974-76 national SO_2 status is shown by second highest 24-hr. average concentration. Asterisks denote counties for which this level exceeded 365 μg/m³. (The current 24-hr. primary standard is 365 μg/m³, which is not to be exceeded more than once per year. Alaska and Hawaii reported no such exceedences.)

Source: Monitoring and Reports Branch, Monitoring and Data Analysis Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency.

TABLE 5-3. ELEVEN SO_2 MONITORING SITES WITH THE HIGHEST ANNUAL MEAN CONCENTRATIONS IN 1978 (VALID CONTINUOUS SITES ONLY)

Location	Annual Means, $\mu g/m^3$	Maximum 24-hr, $\mu g/m^3$	Description
Helena, Deer Lodge Co., MT	152	2512	Rural mine smelter
Pittsburgh, PA	140	602	Center-city industrial
Helena, Deer Lodge County, MT	95	1450	Rural industrial, 1.6 miles east of smelter
Magna, Salt Lake Co., UT	93	811	Suburban industrial
Toledo, OH	84	915	Center-city industrial
Pittsburgh, PA	79	376	Suburban industrial
Buffalo, NY	78	267	Suburban industrial
Kellogg, Shoshone Co., ID	78	294	Suburban residential
Shoshone Co., ID	77	493	Suburban industrial
New York City, NY	77	296	Center-city residential
Mingo Junction, OH	76	329	Center-city industrial

Note: 1 ppm SO_2 = 2620 ug/m^3.

Source: SAROAD.

one or more monitoring sites (for example, Deer Lodge County, MT), but it is likely that there are substantial gradients across the county and almost certainly across an air quality control region (AQCR).

5.2.4 Peak Localized Sulfur Dioxide Concentrations

5.2.4.1 1978 Highest Annual Average Concentrations--The reasons for variability in ambient air SO_2 levels have been mentioned in earlier sections. This section examines United States locations with highest annual averages and highest maximum concentrations and analyzes the distribution of SO_2 concentrations nationally by site descriptors. However, because of the differences in SO_2 concentrations between bubbler and continuous monitoring, the distributions by site descriptor will be treated separately for each method.

Table 5-3 lists annual mean and maximum 24-hour concentrations for the 11 valid continuous monitoring sites in the United States with the highest annual means in 1978. The highest annual mean concentration was 152 $\mu g/m^3$, at a site in Montana 2 miles northeast of a smelter. That site also had the highest 24-hour concentration (2512 $\mu g/m^3$) of any valid continuous monitor. The maximum hourly level was 7205 $\mu g/m^3$, and the second highest hourly level was 6026 $\mu g/m^3$ at this site. Of the highest 11 sites, 5 were associated with smelters, 5 were associated with industrialized areas or towns, and one (New York City) was a densely populated city. In New York City, SO_2 emissions from space heating, power plants, and a variety of industrial sources resulted in a high annual mean concentration. These were peak reporting sites; the urban sites do not typify an entire city. Conversely, even higher concentrations may exist in unmonitored neighborhoods.

5.2.4.2 1978 Highest Daily Average Concentrations--About 50 monitoring sites in the United States have consistently reported maximum 24-hour average SO_2 levels in excess of 300 $\mu g/m^3$ in recent years. Almost all of these have had very high second and third highest values also. Many of the sites having high daily averages were located near specific industrial sources such as smelters, steel plants, and paper mills. Monitors around smelters have frequently reported 24-hour values of 1000 to 3000 $\mu g/m^3$, the highest levels in the United States.

In 1978, high 24-hour SO_2 values occurred in 17 States encompassing all major regions of the country. Ten of the highest sites were in Montana, six were in Wisconsin, and six in Minnesota. Most of these were close to intense sources. However, several urban sites, especially center-city sites in industrialized communities such as Philadelphia and Pittsburgh, PA; New York, NY; Toledo, OH; and Hammond, ID, still have high maximum 24-hour values, above 250 to 300 $\mu g/m^3$.

5.2.4.3 Highest 1-hour Sulfur Dioxide Concentrations-1978 National Aerometric Data Bank (NADB) Data--Single hourly SO_2 values greater than 1000 $\mu g/m^3$ (0.4 ppm) have been measured in about 100 cities and counties in 28 States in recent years. Such values were very widespread across the country; Maine, Florida, Montana, Texas, Arizona, and Washington all had sites in this category. Of these top 100 sites, all except 15 also had second highest values in excess of 1000 $\mu g/m^3$.

Hourly measurements this high are comparatively infrequent and for most of these 100 high sites, less than 1 percent of hourly values were in this category. But for a few sites, notably those close to metal-smelting operations in a few cities, such values were observed up to 5 percent of the time. Highest 1-hour values were found in Deer Lodge County, MT, where several measurements over 5000 $\mu g/m^3$ were recorded at two sites in 1978. Anaconda, MT; Miami and San Manuel, AZ; Newark, DE; Buffalo County, WI; and St. Charles County and North Kansas City, MO, all reported at least one value in excess of 4000 $\mu g/m^3$.

5.2.5 Temporal Patterns in Sulfur Dioxide Concentrations

5.2.5.1 Diurnal Patterns--In some locations, SO_2 concentrations have distinct temporal patterns. These patterns depend on the variability of meteorological factors and on the variability of source emissions.

Diurnal variations in SO_2 concentrations reflect the changing dispersion characteristics of the lower atmosphere and variations in mixing height. If emissions are predominantly from low-level sources such as residential and institutional space heating, the highest hourly concentrations will frequently occur at night and in the early-morning hours. At these times, low mixing height and decreased windspeeds lead to higher concentrations. During the day more vertical mixing usually occurs and windspeeds increase, diluting low-level emissions. Figure 5-4 gives the composite diurnal pattern of hourly concentrations for SO_2 for the month of December 1978 in Watertown, MA. The pattern just described is apparent.

In locations where SO_2 emissions from taller stacks are the major SO_2 source, a different diurnal pattern can occur. In these situations, typical of power plants and smelters, the highest concentrations usually occur in the morning hours just after sunrise. Levels can be almost zero at night if the source is emitting into a stratified region above a lower level inversion. Upon inversion breakup, when heating at the surface causes vertical mixing, an elevated plume can be mixed to the ground. Fumigation conditions lasting from several minutes to several hours can occur. Montgomery and Coleman (1975) analyzed the effects of tall stacks on the peak-to-mean ratios for different averaging times and discussed the influence of inversion breakup. In essence, even with tall stacks, inversion breakup that catches the plume and brings it to the surface can occur. So the peak-to-mean ratio is almost independent of stack height. The frequency of occurrences of fumigation, on the other hand, would most likely be less with taller stacks.

Some similarity can be found in comparing the diurnal pattern of hourly averages for Watertown, MA (Figure 5-4) and St. Louis, MO (Figure 5-5). In February 1977, a major local source of SO_2 was still in operation in St. Louis. The midmorning and late night maxima were again associated with diurnal variations of meteorological factors. By February 1978, the source had shut down, and the reported SO_2 levels at the monitoring stations reflected this fact. The absence of low-level stacks emitting into a stable layer of air near the surface at night was noticeable. Concentrations did not build up at night as in the previous year.

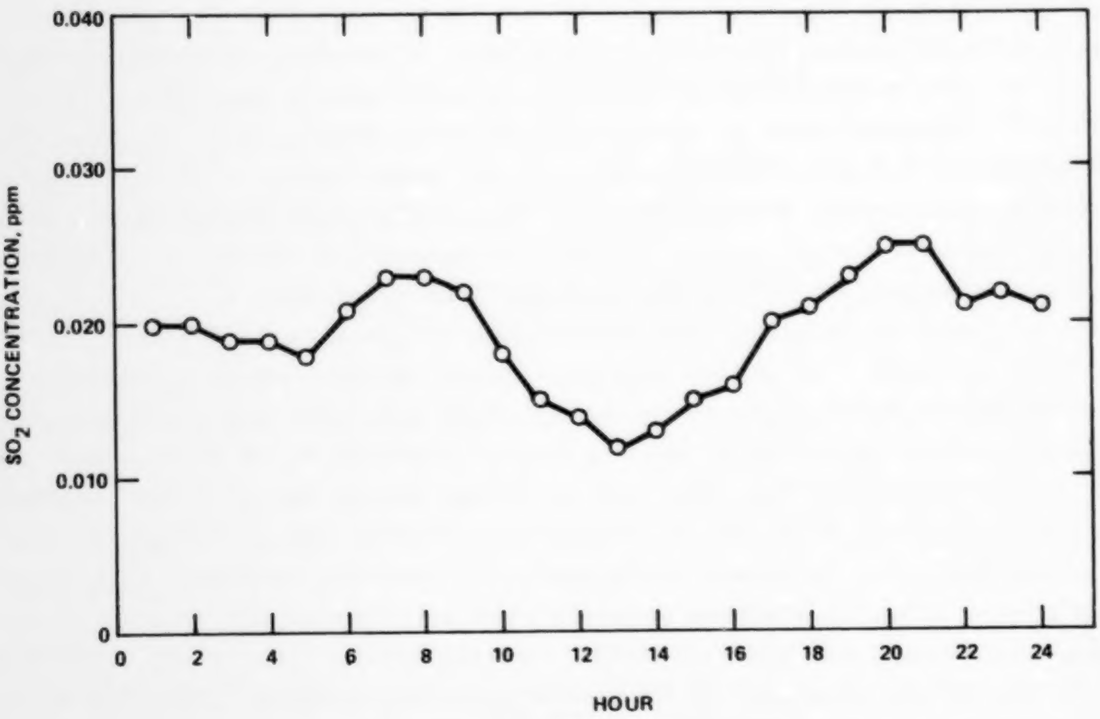

Figure 5-4. Composite diurnal pattern of hourly sulfur dioxide concentrations are shown for Watertown, MA, for December 1978.

Source: Spengler (1980).

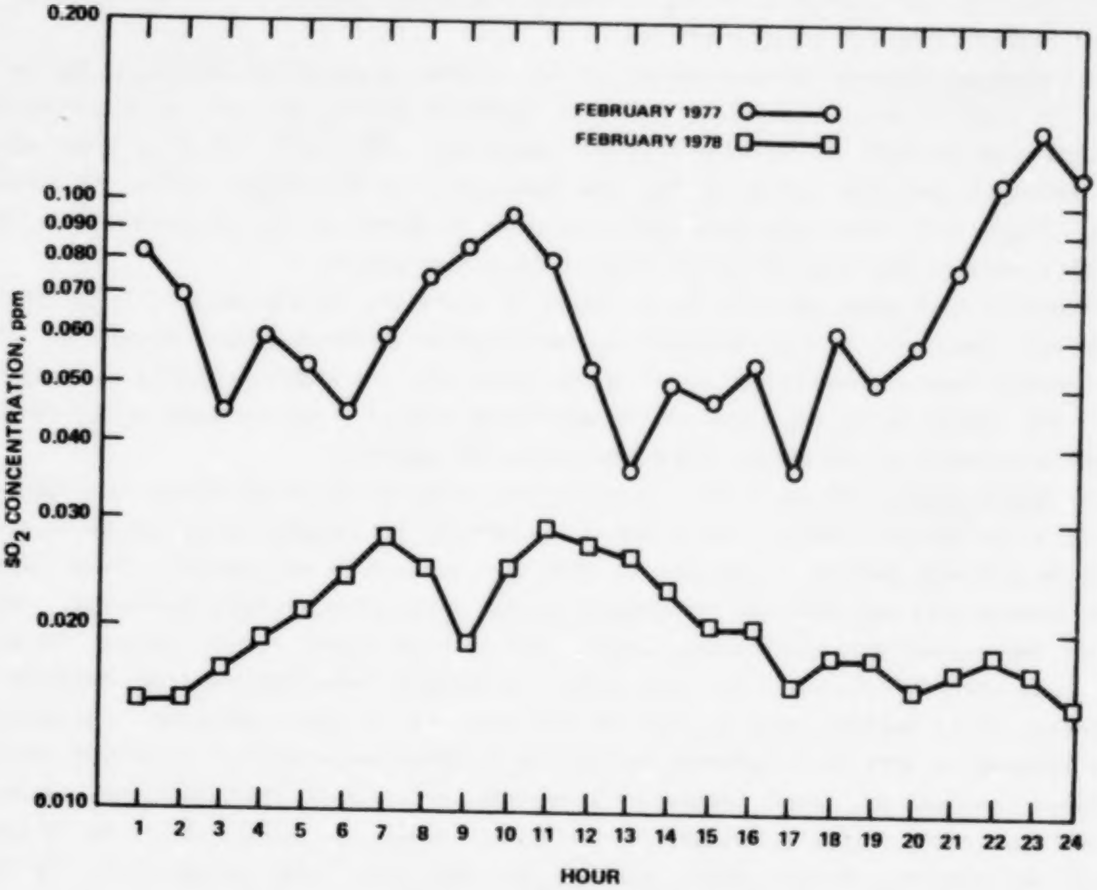

Figure 5-5. Monthly means of hourly sulfur dioxide concentrations are shown for St. Louis (city site no. 26-4280-007, "Broadway & Hurck") for February 1977 and 1978.

Source: Spengler (1980).

Diurnal patterns of hourly SO_2 values for the industrialized river valley town of Steubenville, OH, are shown in Figure 5-6. In June 1976, a distinctive maximum in the diurnal pattern appeared. In July 1977, there was no apparent variation across the hours.

In conclusion, it can be said that the variations in hourly concentrations are influenced by source configuration and meteorological dispersion. Therefore, it is difficult to generalize about diurnal patterns of hourly SO_2 concentrations. Although there may be some similarities, the daily patterns in SO_2 concentrations are different for different locations and can change in time for a given location.

5.2.5.2 Seasonal Patterns--Concentrations of SO_2 display seasonal variability. The variability is most pronounced in areas in which there is strong seasonal variation in the emission-source strength or in meteorological conditions. Obviously, in urban areas where space heating is the major source of SO_2, the levels will be much higher during the heating season. Figure 5-7 illustrates just such situations in Watertown, MA and Steubenville, OH. The highest monthly mean concentrations occur in the winter months.

Figure 5-7 also shows the data for St. Louis, MO where the seasonal pattern is different. Here a local industrial source dominates SO_2 concentration patterns around the monitor. The higher monthly mean concentrations occur in the months with the higher frequency of southerly winds. The source is to the south of the monitoring station. Any increase in SO_2 concentrations as a result of the winter heating season is not apparent.

5.2.5.3 Yearly Trends--The SO_2 levels in most urban areas in the United States have improved steadily since the mid-1960's. The trend of decreasing SO_2 concentrations can be resolved into three distinct periods. From 1964 to 1969, the improvement was gradual. In the middle period, between 1969 and 1972, the improvement in most urban areas was more pronounced. Since 1973 the improvement has again become slower. The 1977 EPA trends report states: "In most urban areas, this is consistent with the switch in emphasis from attainment of standards to maintenance of air quality; that is, the initial effort was to reduce pollution to acceptable levels followed by efforts to maintain air quality at these lower levels." From 1972 through 1977 annual averaged SO_2 levels dropped by 17 percent, or an annual improvement rate of about 4 percent per year. Figure 5-8 summarizes the annual average SO_2 concentrations for 32 urban National Air Sampling Network (NASN) stations for the years 1964 through 1971. In this figure, the first two periods are apparent. In Figure 5-9, the national trends in annual average SO_2 concentrations from 1972 through 1977 at 1233 sampling sites are displayed. In this figure, the diamond symbolizes the composite annual average concentration; the triangle is the median value, while the circles are extreme values and the thick band covers the 25th to 75th percentile range.

Over the period of 1970 through 1977, SO_2 emissions have decreased only slightly (U.S. Environmental Protection Agency, 1978). In 1970 the estimated annual manmade SO_2 emissions were 29.8 million metric tons. By 1977 this was reduced to 27.4 million metric tons. The improvement in the ambient air quality levels for SO_2 reflected the displacement of sources from urban areas to rural areas, restriction of sulfur content of fuels used by low-level

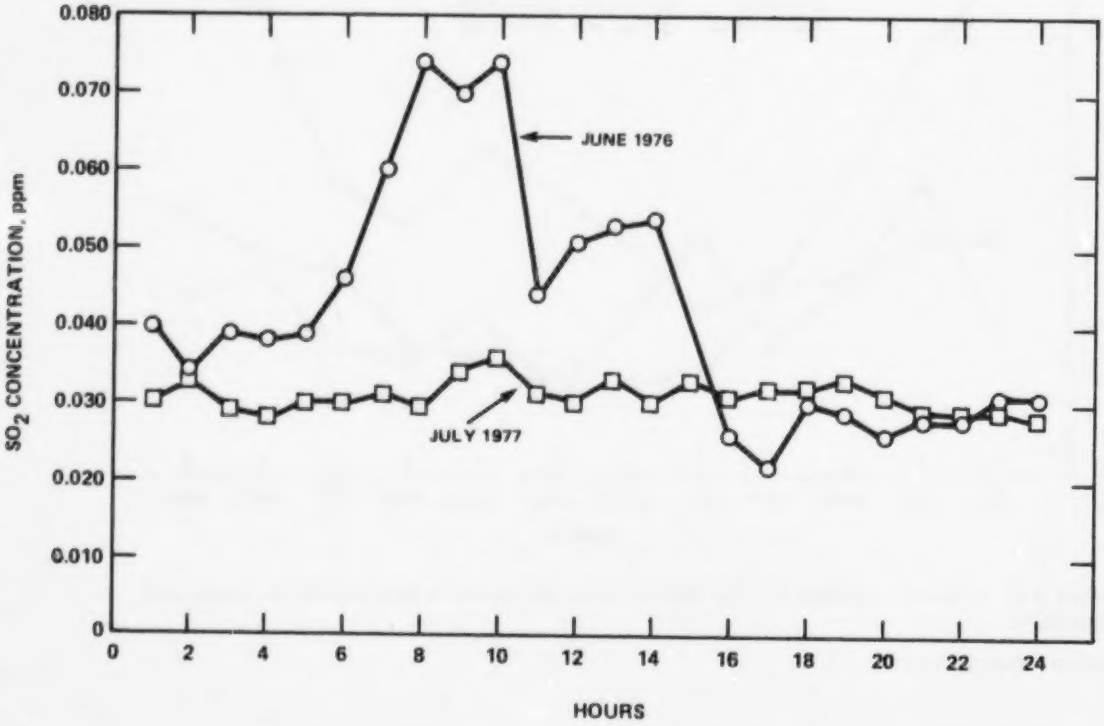

Figure 5-6. Monthly means of hourly sulfur dioxide concentrations are shown for Steubenville, OH (NOVAA site 36-6420-012) for June 1976 and July 1977.

Source: Spengler (1980).

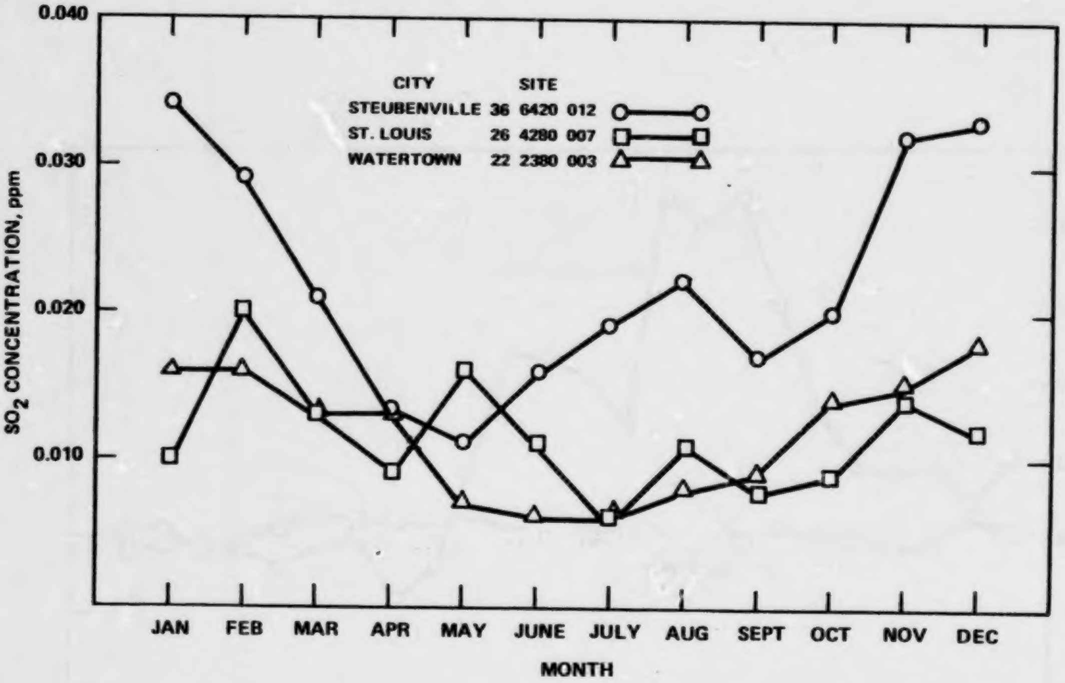

Figure 5-7. Seasonal variations in sulfur dioxide levels are shown for Steubenville, St. Louis, and Watertown.

Source: Spengler (1980).

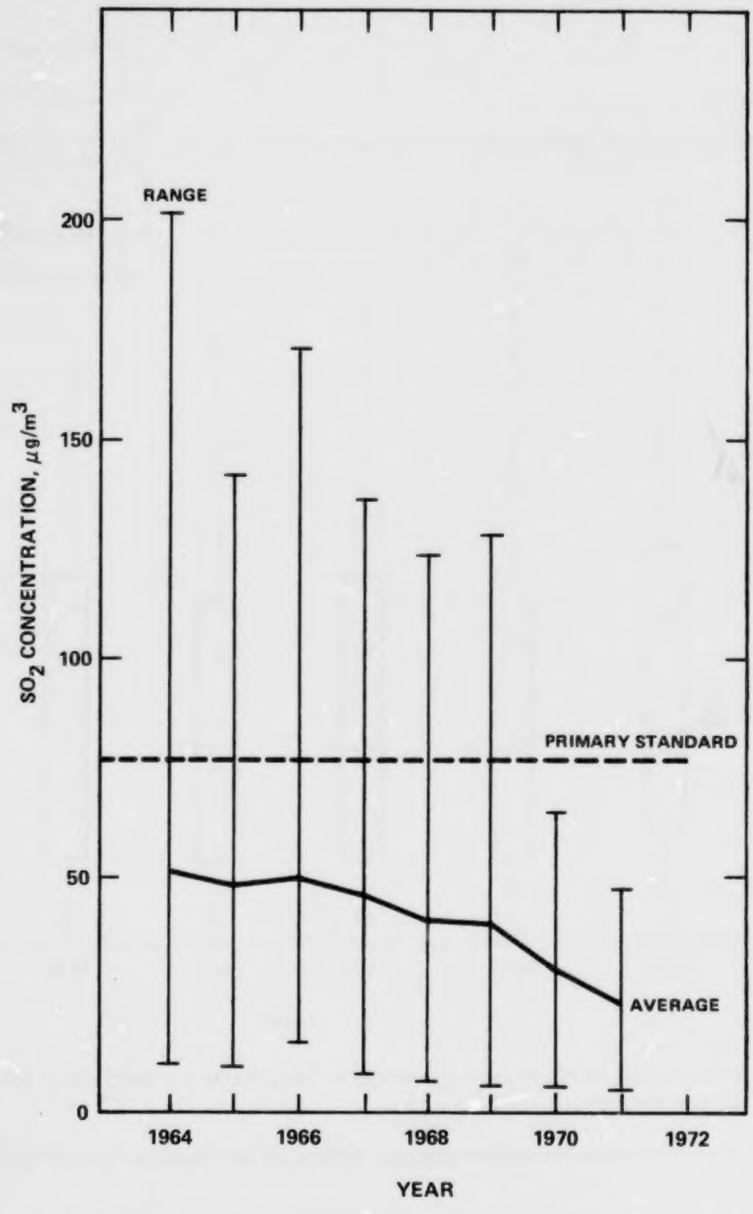

Figure 5-8. Annual average sulfur dioxide concentrations are shown for 32 urban NASN stations.

Source: National Academy of Sciences (1975).

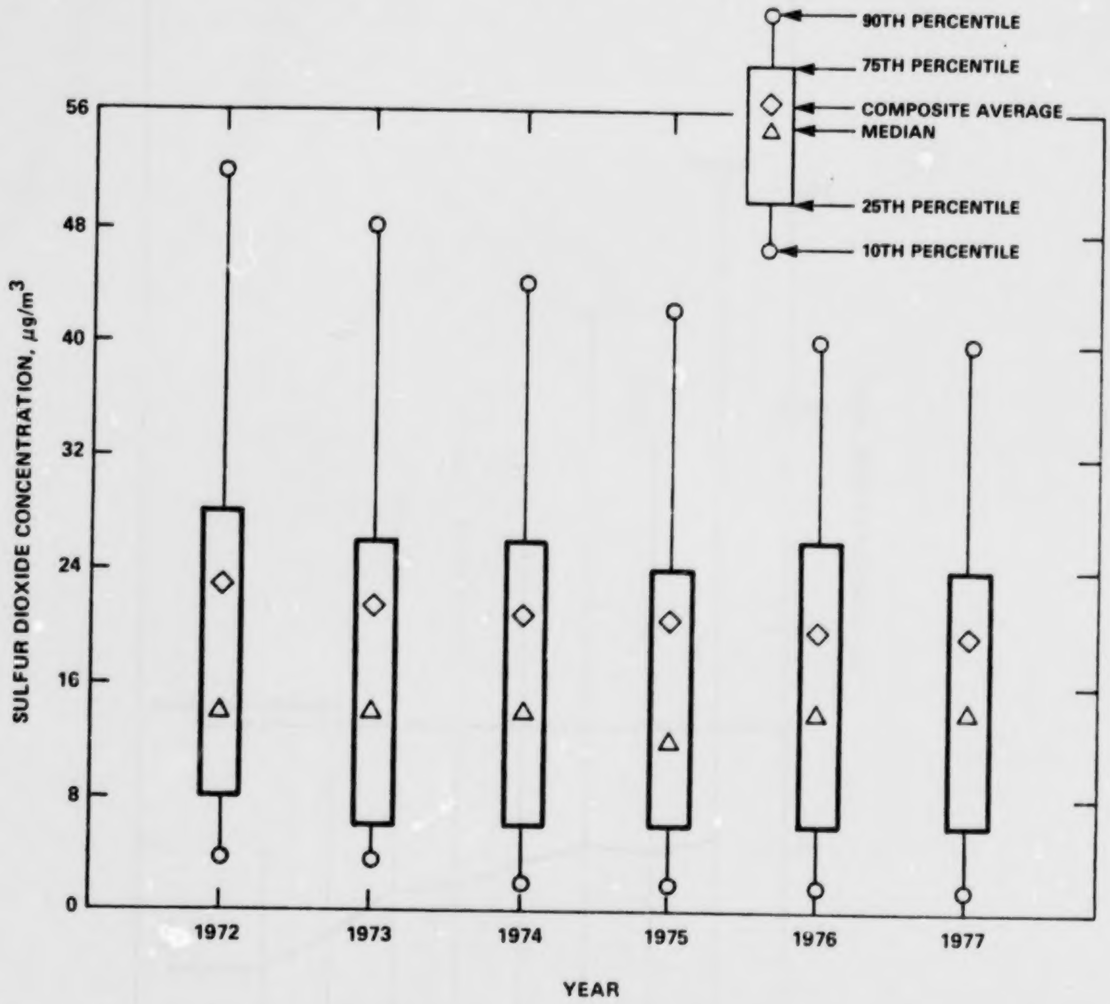

Figure 5-9. Nationwide trends in annual average sulfur dioxide concentrations from 1972 to 1977 are shown for 1233 sampling sites.

Source: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards (1978a).

area sources, building of sources with taller stacks, and source emission controls.

The first air quality criteria document for SO_x, published in 1969, presented the frequency distributions for SO_2 levels in selected American cities for 1962 through 1967 (National Air pollution Control Administration, 1970). The 1960's data came from the Continuous Air Monitoring Project (CAMP), which operated continuous monitors in a few of the largest U.S. cities: Chicago, Philadelphia, St. Louis, Cincinnati, Los Angeles, and San Francisco. Improvements in SO_2 levels in each of the six cities are demonstrated by comparing 1962 to 1967 data with data for 1977 (Table 5-4). In each city there is more than one continuous monitor now operating. The station reporting the highest levels in 1977 was used in order not to overemphasize any improvement. The comparison is only an approximation because the locations of the monitors and the instrumental methods used were not the same as those reported in the 1969 document.

In each city the peak concentration decreased. In most cities the 1977 peak was less than one-half the earlier values. The only exception was St. Louis, where the earlier peak was 0.72 ppm and the 1977 peak was 0.67 ppm. The result was not unexpected in that the earlier summary was a composite frequency distribution of 5 years of monitoring.

TABLE 5-4. COMPARISON OF FREQUENCY DISTRIBUTION OF SO_2 CONCENTRATION (PPM) DURING 1962-67[a] AND DURING 1977[b]

City	Year	Frequency Distribution of SO_2 (ppm)					
		Percentile 30	50	70	90	99	Maximum
Chicago	1962-67	0.03	0.08	0.17	0.32	0.65	0.95
	1977	0.01	0.02	0.03	0.06	0.12	0.25
Philadelphia	1962-67	0.03	0.05	0.09	0.21	0.45	0.85
	1977	0.01	0.02	0.04	0.08	0.23	0.44
St. Louis	1962-67	0.02	0.03	0.05	0.11	0.26	0.72
	1977	0.01	0.01	0.03	0.10	0.37	0.67
Cincinnati	1962-67	0.01	0.02	0.03	0.07	0.18	0.53
	1977	0.01	0.02	0.02	0.04	0.08	0.29
Los Angeles	1962-67	0.01	0.01	0.02	0.04	0.08	0.25
	1977	0.01	0.02	0.02	0.03	0.05	0.09
San Francisco	1962-67	--	--	0.01	0.03	0.07	0.17
	1977	--	0.001	0.01	0.01	0.03	0.03

[a] Concentrations from CAMP stations as reported in Air Quality Criteria for Sulfur Oxides, National Air Pollution Control Administration (1970).

[b] Concentrations from National Aerodynamic Data Base (1977).

Note: 1 ppm SO_2 = 2620 ug/m^3.

More stable indicators of improved air quality are provided by the 50th, 70th, and 90th percentile concentrations. In Chicago, the 50th percentile concentration dropped from 0.08 ppm to 0.022 ppm. In Philadelphia, the levels improved substantially; the 50th, 70th, and 90th percentile concentrations were less than one-half the earlier values. St. Louis and Cincinnati showed modest improvement; their 50th percentile concentrations were lower in 1977 than they were in the mid-1960's. The highest concentrations occurred as frequently in St. Louis as they did earlier, but in Cincinnati they occurred less frequently. Review of the St. Louis SO_2 data showed improved air quality for most of the city. The high concentrations reported in 1977 were typical of only a small section of the city. Los Angeles showed improvement in reducing the high concentrations, but the 50th percentile concentration was actually slightly higher in 1977 than it was in the previous decade. Similarly, San Francisco trimmed the peaks but had a very low median value.

In summary, the frequency of peak levels has been reduced in most urban areas. The steady improvement of SO_2 ambient air quality has been slowed somewhat in recent years. Only 1 percent of the SO_2 monitoring sites show levels above 80 $\mu g/m^3$, the current annual NAAQS. In 1974, the annual mean SO_2 standard was exceeded in 3 percent of the monitoring stations (31 of 1030), compared with 16 percent in 1970. In 1977 and 1978, 2 percent of the sites reported violations of the 24-hour standard. In 1974, this standard was exceeded in 4.4 percent of the reporting stations (99 of 2241), compared with 11 percent in 1970. Many of these sites reporting violations of the 24-hour standard are in remote areas near large point sources.

5.3 AMBIENT MEASUREMENTS OF SUSPENDED PARTICULATE MASS

The general character of airborne matter designated as atmospheric suspended particles has been described in Chapter 2. These particles range in size from about 5×10^{-9}m, roughly corresponding to agglomerates of a few tens or hundreds of molecules, up to about 10^{-4}m, specks of material discernable to the human eye. A useful division of these particles by size into fine and coarse fractions occurs in the range of 1 to 2×10^{-6}m or 1 to 2 μm, as was discussed in Chapter 2.

The mass of suspended particles, generally concentrated in particles above about 0.1 μm, is usually estimated by filtration of known volumes of air. The goal of this filtration process is the separation of the gas phase from liquid and solid condensed phases of atmospheric aerosol. Thus, the mass of material accumulated on a filter is taken to represent the volume of aerosol filtered, and results are presented as μg of PM/cubic meter of aerosol, abbreviated $\mu g/m^3$.

Chapter 3 discusses some of the complications of commonly used filtration methods, including retention of reactive gases such as SO_2 and HNO_3 and loss by evaporation of water and other moderately volatile substances. While commonly used filtering media are highly efficient for collection of fine particles, samplers of coarse-particle concentrations have had major design defects. Despite these complications, which were discussed in detail in Chapter 3, the largest body of information on the distribution of suspended PM in time and space has been obtained with the hi-vol, or TSP method. Routine monitoring information is available from the NADB maintained by EPA for many sites. Some are EPA sites; many are operated by State and local agencies.

The following discussion relies mainly on NADB data; additional analyses are to be found in the 1976 and 1977 National Air Quality and Emissions Trends reports, in Trends in the Quality of the Nation's Air reports in 1980, and in the document Deputy Assistant Administrator's Report on Ambient Monitoring Activities - Air Portion. (U.S. Environmental Protection Agency, 1977; 1978; 1980a; 1980b).

5.3.1 Monitoring Factors

The accuracy and precision of PM monitoring are limited by three general considerations: sampling methods, including instrumentation, analytical methods, and quality assurance; sampling frequency; and location of monitors. Chapter 3 discusses the first of these considerations; the second and third are discussed in this chapter. Sampling frequency affects the confidence limits on mean TSP concentrations and annual or seasonal trends. It is appropriate to discuss this limitation at the beginning of this section before the 1978 national TSP data base is presented. The siting of particle monitors significantly influences the levels measured and, hence, the interpretation of data. These considerations are presented with examples in several sections of this chapter.

5.3.1.1 Sampling Frequency--In 1978, there were 4105 TSP monitoring sites in the United States and its territories that reported data to the NADB of the U.S. EPA. Of these, only 2882 had enough observations per quarter and per year for the data to be considered valid for estimating annual averages. The number of sites reporting valid data ranged from zero in Delaware and American Samoa to 318 in Ohio. The most populous states, California and New York, had 60 and 236, respectively.

The U.S. EPA has established a uniform sampling schedule to be followed by all State and local agencies. It requires a 24-hour sample (midnight to midnight) every sixth day. Hence, in 1 year there are 60 or 61 possible sampling days from which to derive the mean value and distribution, and to determine attainment of current standards. In 1978, 14 percent of all reporting sites had 60 or more observations.

Sampling days are missed and samples must be voided for a variety of reasons. Therefore, a minimum requirement has been established for considering the data from any site as valid in determining an annual average: There must be at least five observations during each quarter of a calender year. Of the Federal, State, and local TSP sites reporting data to NADB, 70 percent met this requirement.

The distribution of observations for the 2882 valid monitoring sites in 1978 is shown in Figure 5-10. Of these sites, 10 percent had less than 47 observations and 50 percent had more than 56 observations. However, 90 percent of the monitoring sites collected fewer than 60 samples. Three percent of the monitors sampled at an equivalent frequency of 1 day in 3, and fewer than 2 percent collected samples at a frequency of 1 day in 2.

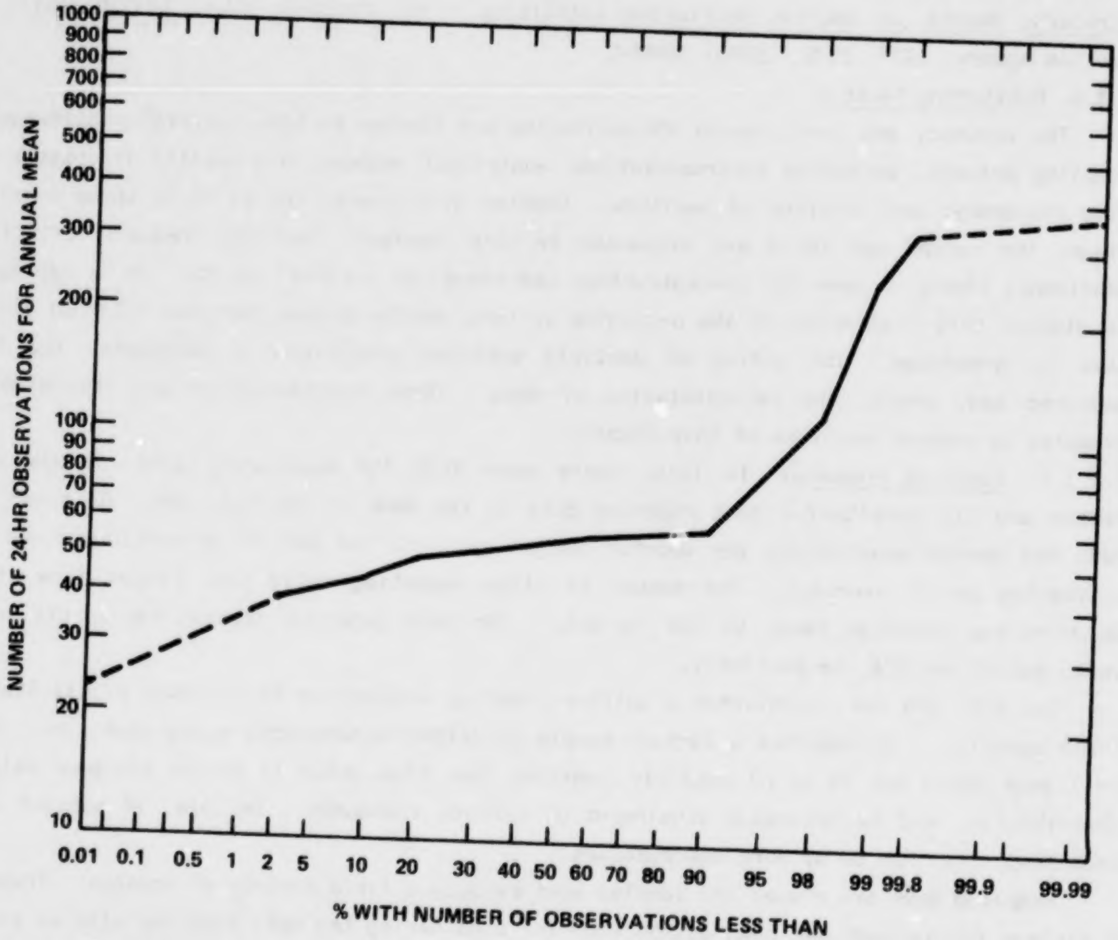

Figure 5-10. Distribution shows the number of TSP observations per valid site in 1978; total is 2882 sites.

Source: SAROAD.

The current NAAQS for TSP consists of an annual geometric mean and a once-per-year daily value. Frequency of monitoring is a fundamental parameter of the air quality data used for comparison with the standards. The period of determining an annual average for comparison is a calendar year. If the number of 24-hour observations is less than 365, then the true mean concentration for the year can only be expressed as residing within a range of values. On the assumption that the actual distribution of values is log normal, confidence intervals can be calculated from the geometric mean and the geometric standard deviation. Figure 5-11 shows the effect of sample size on the 95-percent confidence intervals for a hypothetical site whose true annual geometric mean is equivalent to 75 $\mu g/m^3$, the current annual standard. From this example, we can only conclude that with 95 percent probability the annual geometric mean is between 67 and 85 $\mu g/m^3$, if the mean for that year was determined from a sample size of 61. Increasing the sampling frequency to 1 day in 2 reduces the level of uncertainty so that the annual mean is known to lie between 70 and 81 $\mu g/m^3$. Thus, by increasing the sampling frequency by a factor of three, the width of the 95-percent confidence interval for the true annual geometric mean has been cut by a factor of 1.7 (square root of 3).

A critical factor in evaluating compliance with once-a-year standards is the effect of sampling frequency. Figure 5-10 shows that in 1978 the majority of valid sites (80 percent) had fewer than 60 sampling days. The sites with more frequent sampling had a greater chance of sampling the higher concentrations (Figure 5-11). Assuming that there are a number of days on which the observations are above the standards, the probability of selecting 2 or more days on which standards are exceeded is a function of sampling frequency. If there are 10 days above the standards, there is only a slightly better than 50-percent chance of actually monitoring on 2 of those days given a sampling frequency of 61 out of 365 days. When the sampling frequency is doubled to 122 sampling days, the probability of capturing 2 days out of 10 that exceed the standards increases to 80 percent. In actuality, samples are not taken randomly; they are taken systematically, usually at a rate of once every 6 days. The probability of capturing the highest period is further complicated in that the log normal distribution of TSP concentrations does not apply uniformly to all sites.

An additional complication in determining compliance or trends occurs when the meteorological regimes affecting the TSP concentrations are considered. Attainment of standards may depend on the number of "clean" sampling days versus the number of "dirty" sampling days. Watson (1979) exemplifies this problem with Portland, OR, TSP data. The annual geometric mean TSP data show a decreasing trend from 1973 through 1975, with a significant increase in 1976. If these data are reexamined and weighted by the meteorological regimes actually sampled in each year, the conclusions are changed. The stratified mean TSP values show a large drop in concentrations occurring between 1974 and 1975; the levels are constant for the years before and after. Since these means are determined from a sample set varying from 49 samples in 1974 to 79 samples in 1976, a statistical test is required to determine whether the means of any year are significantly different from those of any other year. The 95-percent confidence

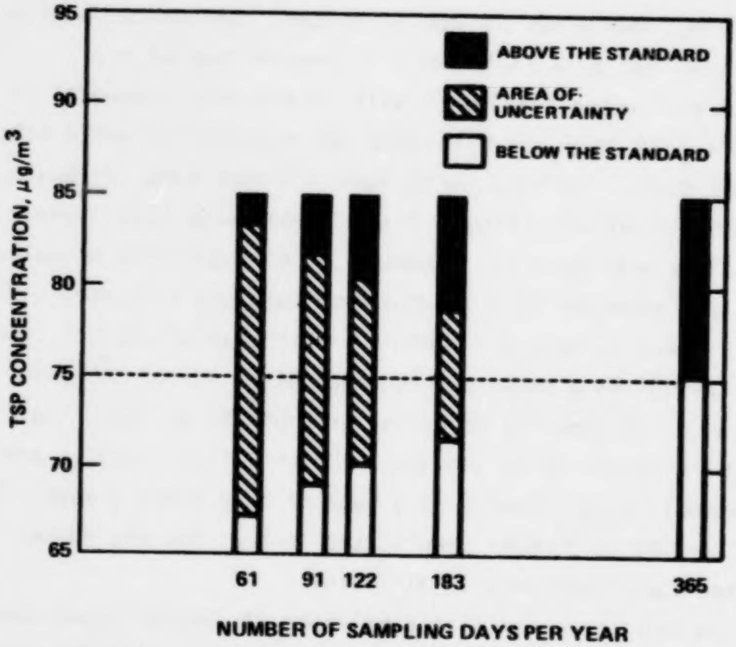

Figure 5-11. The 95 percent confidence intervals about an annual mean TSP concentration of 75 $\mu g/m^3$ is shown for various sampling frequencies (assume the geometric standard deviation equals 1.6).

Source: Curran and Hunt (1975).

intervals for all stratified means do overlap. Watson concludes, then, that there is a reasonable chance that the true means do not really vary from year to year.

5.3.1.2 Monitor Location--The choice of sampling location can obviously affect the concentrations measured. Remotely located monitors typically record low concentrations; urban monitors characteristically record higher concentrations. The positioning of a monitor at a chosen location can also affect measured concentrations. For example, at a specific location, the height of the monitor above the ground influences sample concentrations. If the monitor is elevated above surface sources, lower concentrations of coarser particles might be measured. Some studies clearly indicate that TSP concentrations decrease with increasing monitor elevation (Record and Bradway, 1978; Record et al., 1979; Lioy et al., 1980a; Pace et al., 1977), with distance from a roadway, and with distance from other nearby sources.

The inferences drawn about air quality levels, trends, and population exposures from the TSP data presented in this chapter are made in full knowledge of the following limitations of TSP monitoring:

1. Sampling sites are not standardized.
2. Frequency of sampling is quite varied.
3. The majority of sites reporting have fewer than 60 sampling days per year.
4. The frequency of sampling is not weighted with respect to meteorological conditions.
5. No spatial averaging is used in analyzing or reporting data
6. Though the ambient air monitor is stationary, the population it is intended to represent is highly mobile and spends some time indoors.

5.3.2 Ambient Air TSP Values

The distribution of 1978 annual arithmetic means for valid TSP monitoring sites is plotted in Figure 5-12. Half of all the nation's sites had annual arithmetic mean values less than 60 μg/m^3. Annual mean values range from 9 to 256 μg/m^3. Only 14 valid sites had annual mean concentrations equal to or less than 16 μg/m^3. These lower values were recorded in remote monitoring sites. Two background sites, Glacier National Park, MT, and Acadia National Park, ME, had 1977 annual averages of 11 and 21 μg/m^3, respectively. At the other end of the distribution, 25 percent of sites had annual means greater than 76 μg/m^3, and 10 percent were greater than 96 μg/m^3. Higher annual concentrations were found in many populated and industrialized areas. About 30 sites reported annual averages in 1978 above 150 μg/m^3. Topping the list were four central-city sites in commercial, residential, or industrial settings. A Phoenix, AZ, site (0136) had the highest annual mean of 256 μg/m^3, followed by a site in Calexico, CA, at 201 μg/m^3 and an industrial site in Granite City, IL, at 197 μg/m^3.

These extremely high annual TSP concentrations were found in commercial and industrial locations. Of the 30 highest sites, 15 were industrial. Many of the higher concentrations (19 of 30) were found at central-city locations. Only four were classified as rural sites, most of which were also residential areas. It is also likely that arid climates and dusty conditions in the vicinity of some monitoring sites might have led to suspension of surface material. However, it is impossible to ascertain the contribution of fugitive or resuspended

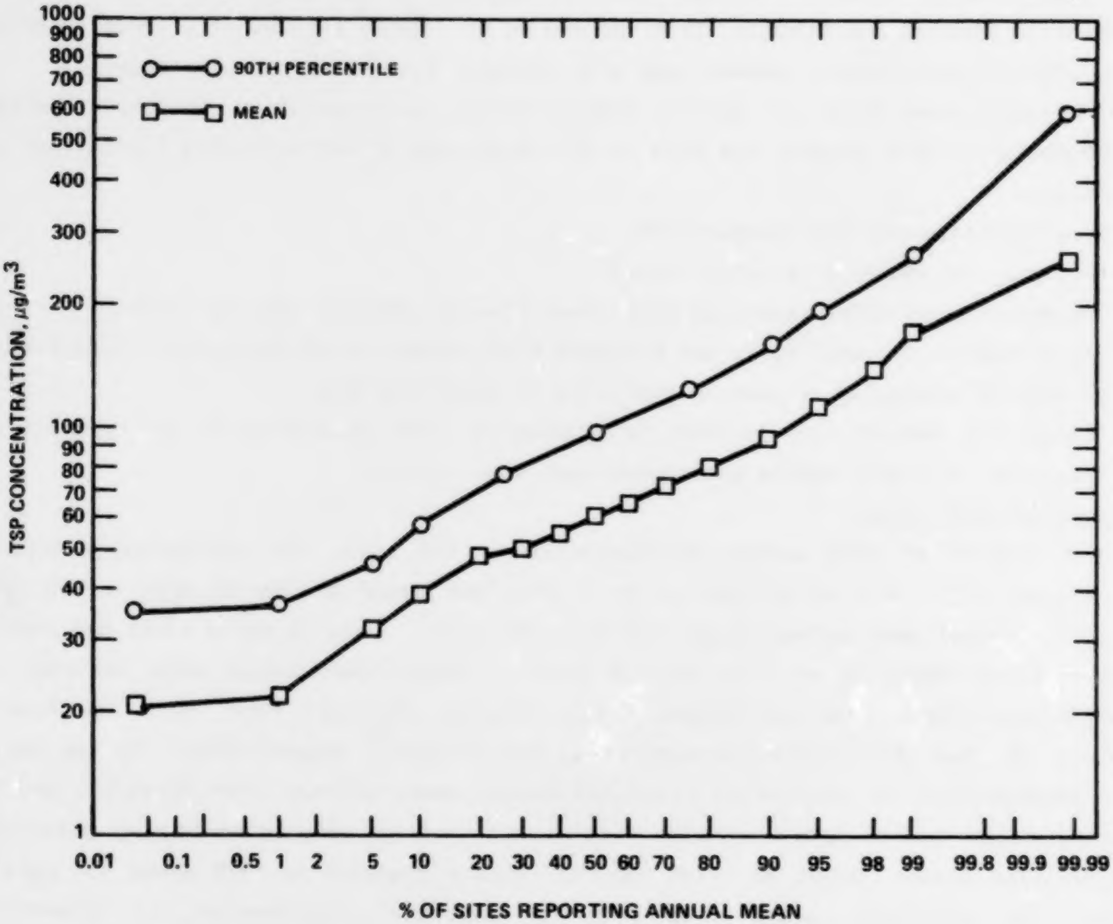

Figure 5-12. Distribution of mean and 90th percentile TSP concentrations is shown for valid 1978 sites.

Source: SAROAD.

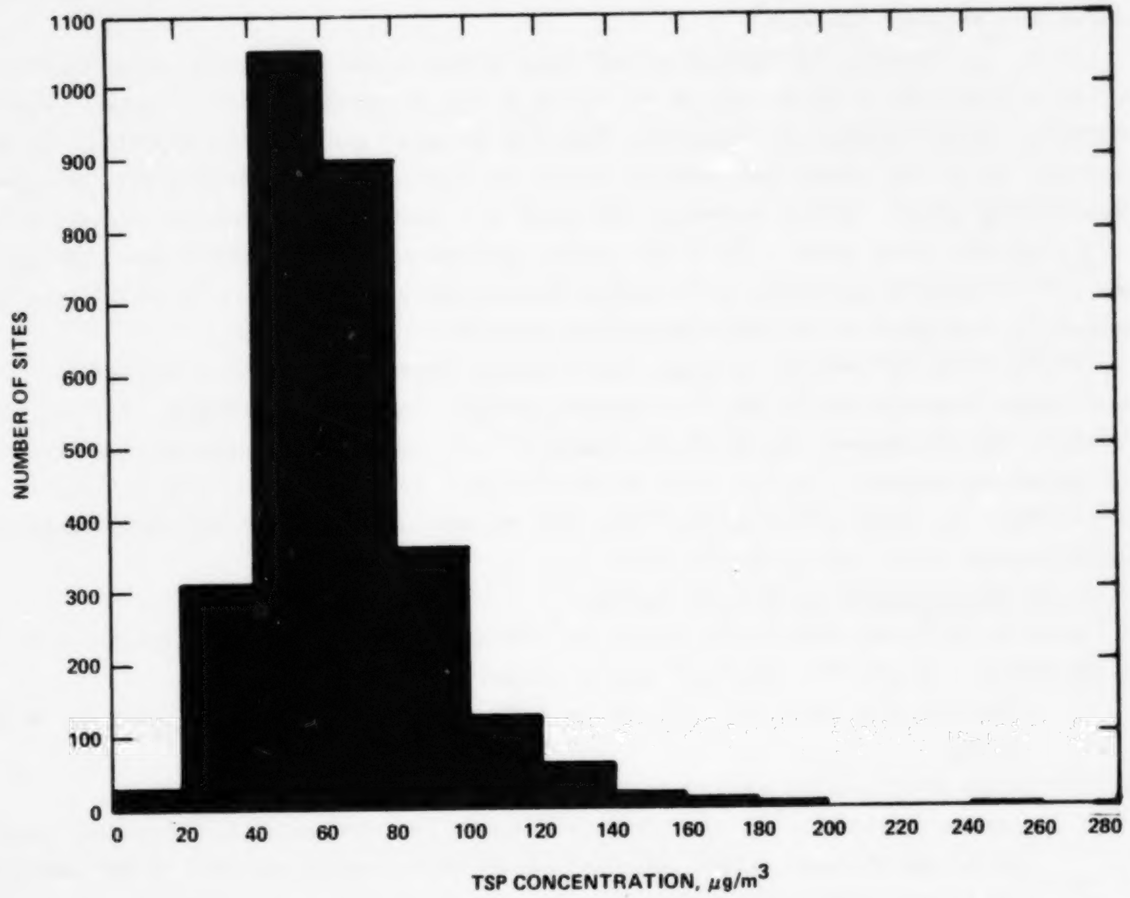

Figure 5-13. Histogram of number of sites against concentration shows that over one-third of the sites had annual mean concentrations between 40 and 60 μg/m³ in 1978.

Source: SAROAD.

dust to the concentrations measured at these 30 sites without more detailed analysis. The histogram of sites against concentrations (Figure 5-13) shows that over a third of all monitoring sites had annual mean values between 40 and 60 µg/m^3. Slightly less than another third had annual averages between 60 and 80 µg/m^3.

The distribution of 90th percentile values is also plotted in Figure 5-12. Half of all valid monitors had a 90th percentile value in excess of 97 µg/m^3. For 10 percent of the monitors, 10 percent of the observations exceeded 160 µg/m^3. For one monitor, 10 percent of the observations exceeded 600 µg/m^3.

Daily, or 24-hour, TSP concentrations have a wide range. In remote areas such as the Pacific Islands, daily values may be as low as a few micrograms per cubic meter. Over the continental United States, concentrations from 5 to 20 µg/m^3 are routinely reported. In other locations, daily TSP values can exceed 10 times the levels found in remote areas, on occasion exceeding 3000 µg/m^3. Values exceeding 1000 µg/m^3 are observed in remote arid regions as well as in populated urban areas. Daily TSP levels approaching these higher values, 500 to 1500 µg/m^3, are frequently associated with adverse meteorological conditions: low-level inversion, stagnation, or high winds resuspending surface material.

Thirty valid TSP monitoring sites report highest 24-hour values above 600 µg/m^3. Only a few of these sites are in the top 30 in annual average. In cities like Topeka, KS, and Libby, MT, which are not densely populated or industrialized, these high concentrations may result from chance occurrences, such as fires or dust storms. In other cities like El Paso, TX, and Granite City, IL, which are industrialized, the maximum concentrations are more likely to be related to persistent sources of pollution.

5.3.3 TSP Concentrations by Site and Region

Airborne particles measured by the hi-vol TSP method arise from many sources, and these are described in Chapter 4. Important source categories include:

1. Fugitive dust emissions stirred up by mechanical action or the wind as in dust storms.
2. Large point sources such as smokestacks.
3. Chemical reactions in the atmosphere that transform gaseous substances, such as sulfur and nitrogen oxides, ammonia, and volatile organic species, to PM substances.
4. Low-level widely dispersed combustion sources such as automobiles and trucks, residential furnaces, fireplaces, and wood stoves.
5. Occasional or sporadic sources that can in some instances cause very high TSP values. Examples are agricultural tilling and burning, wildfires in forests, grasslands or even cities, and roadgrading.

The relative contributions of these sources can vary widely and are influenced by location of TSP monitors relative to potential sources and meteorological conditions. Hence, it is not surprising to see a wide variation in daily measurements at a single site, variation over an urban area, or variation among regions of the country. This section will, by illustration, examine these differences in TSP concentrations by location.

5.3.3.1 TSP by Site Classifications--Evidence that fugitive dust contributes significantly to both western arid sites and many urban sites is quite extensive. Discussion of the general influence of fugitive dust may be found in section 5.6.4, below.

The general differences in annual TSP concentration among locations are seen in Figure 5-14. These differences reflect the character of the neighborhoods where the monitors are located. This figure summarizes the mean concentrations from 154 sites in 14 cities. Residential neighborhoods in and near cities have TSP levels between 50 and 70 $\mu g/m^3$. Commercial sites have a wider range of concentrations (60 to 110 $\mu g/m^3$). Industrial locations generally range between 80 to 150 $\mu g/m^3$.

The 1978 data base also has been analyzed on the basis of two additional sets of descriptors. One description scheme classifies monitoring sites by their purpose: population exposures, source receptors, or background sites. The other scheme identifies sites by the amount of development: central-city, suburban, rural, or remote. These classifications are not mutually exclusive.

When sites are grouped by descriptors, a distinct weighting becomes apparent. Almost 80 percent of the sites are population oriented; approximately 15 percent are source related, and less than 6 percent are background monitors. The distribution by development also reflects its population emphasis. Of the total monitors, 83 percent are at either central-city or suburban sites, 15 percent are at rural sites, and 2 percent are at remote sites. In these data, 38 percent of the background sites had median values less than or equal to 27 $\mu g/m^3$, whereas only 4.4 percent of all sites had these low values. Only 30 percent of the background sites had median values above 44 $\mu g/m^3$ (none had values above 97 $\mu g/m^3$), whereas 75.5 percent of source sites had median values above 44 $\mu g/m^3$. The pattern is consistent for the distribution of the 90th percentiles cross-tabulated by site purpose. Cross-tabulations of site median values and site 90th percentile values with the development-related site descriptors is further confirmation of the influence of location on measured TSP concentrations. Rural and remote sites have lower median values and lower 90th-percentile values. The suburban sites reflect the overall national distribution. The central-city category has proportionately more sites in the higher concentration ranges.

5.3.3.2 Intracity Comparisons--Because of the strong neighborhood influence on TSP concentrations, it is not unusual to find considerable variation in peak and mean concentrations across a community. Examination of intracity differences illustrates the difficulty in estimating population exposures to TSP.

Data on the nine cities having the highest annual TSP concentrations in 1977 are given in Table 5-5. Only sites having enough observations per quarter to report an annual mean are used. Although TSP concentrations in these cities were generally high, in 1977 the less developed or less industrialized areas in each city had annual geometric mean concentrations below 75 $\mu g/m^3$, (currently the annual primary NAAQS), with the exception of Granite City, IL.

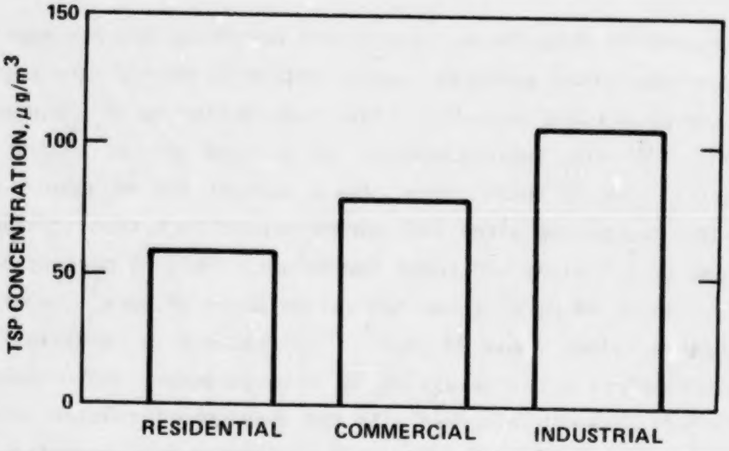

Figure 5-14. Histogram of mean TSP levels by neighborhood shows lowest levels in residential areas, higher levels in commercial areas, and highest levels in industrial areas.

Source: Office of Air Quality Planning and Standards (1976).

TABLE 5-5. RANGE OF ANNUAL GEOMETRIC MEAN CONCENTRATIONS IN AREAS WITH HIGH TSP CONCENTRATIONS IN 1977

City	Number of sites	Number of sites with annual average >75 μg/m^3	Annual range, μg/m^3	Range of maximum 24-hr value, μg/m^3
Tucson, AZ	7	3	67-156	178-591
Pocatello, ID	4	3	65-218	344-1371
Chicago, IL	25	12	50-170	152-1106
Granite City, IL	8	8	85-185	227-485
Taos County, NM	1	--	168	577
Middletown, OH	3	2	64-192	157-707
Cleveland, OH	23	13	48-152	128-705
Youngstown, OH	5	4	66-172	163-602
El Paso, TX	14	10	60-158	205-691

The annual mean concentration for the dirtiest sites can be two to four times higher than that for the cleanest sites within the same city.

5.3.3.3 Regional Differences in Background Concentrations--It has been demonstrated that TSP concentrations can vary across an urban area and among cities with different sources and meteorology. In addition, there may be regional differences in the natural or transported fraction of TSP concentrations. Figure 5-15 shows the contribution of these sources to nonurban levels. It was assumed that the global and local contributions in the average would be similar. The greatest difference among regions is the contribution from "continental" and transported emissions. These two categories of particles contribute in such a way that nonurban sites in the West typically report annual geometric means of 15 μg/m^3; in the Midwest, 25 μg/m^3; and in the East, 35 μg/m^3. Except for the Acadia National Park site (18 μg/m^3) and Millinocket (23 μg/m^3), all sites in Maine had 1977 annual geometric means above 30 μg/m^3. Nonurban sites in Wisconsin had mean TSP levels less than 25 μg/m^3. Nonurban sites in Montana had levels less than 20 μg/m^3 in 1977; the individual means were Big Horn County, 17 μg/m^3; Custer County, 15 μg/m^3; and Powder River County, 14 μg/m^3. Such an analysis does not exist for coastal areas in the far West, where densely populated areas cluster thickly and the city-to-city transport component is large.

5.3.3.4 Peak TSP Concentrations--To indicate the severity of TSP ambient exposures, the 90th percentile concentration of the 24-hour measurements was examined for all 4008 sites in the

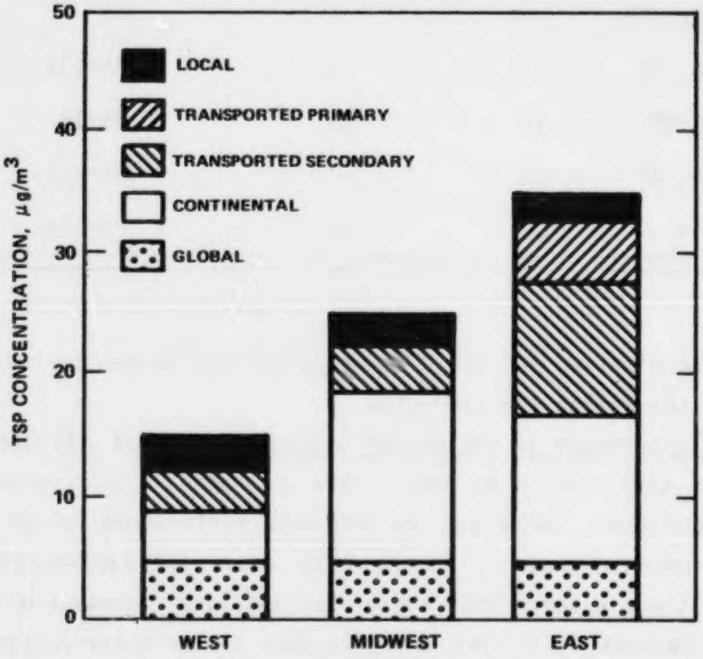

Figure 5-15. Average estimated contributions to nonurban levels in the East, Midwest, and West are most variable for transported secondary and continental sources.

Source: Lynn et al. (1976).

1977 NADB. The concentrations of TSP and other air pollutants had been widely reported to be log normally distributed (Larsen, 1971). This statistical relationship, however, appeared inappropriate at the high and low ends of the distribution (Mage and Ott, 1978). Because the extreme values at the high end are subject to wide scatter, the 95th or 99th percentile was found to be less representative of the severity of high TSP levels. The 90th percentile was therefore chosen as being a more stable indicator, the TSP value which is exceeded 36 days of the year.

Figure 5-16 shows the number of AQCR's where at least one of the monitors had its 90th percentile TSP concentration within the various categories. Of the country's 247 AQCR's, only 21 reported 90th percentile values for all data collected below 100 $\mu g/m^3$. There were 142 AQCR's that had 90th-percentile values at one or more sites, between 100 to 200 $\mu g/m^3$. These data suggest that most of the U.S. population might experience ambient TSP concentrations exceeding 100 $\mu g/m^3$ for at least 36 days of the year.

5.3.4 Temporal Patterns in TSP Concentrations

5.3.4.1 Diurnal Patterns--TSP concentrations vary with local emission strength, meteorological conditions, and changes in contributions from background particles. The particle emissions loadings to the atmosphere generally increase during the day and decrease at night. The atmosphere undergoes greater vertical mixing during the day, and windspeeds near the surface increase as a result. Greater vertical mixing coupled with increased source emissions cause particle mass loadings to increase. At night, decreased mixing and the resultant decreased surface winds permit settling of larger particles. With increased atmospheric stability, local elevated sources are not as likely to mix to the ground. Unfortunately, diurnal cycles are not well established because the standard sampling procedure for TSP measurements yields a 24-hour sample, midnight to midnight.

Trijonis et al. (1980) found no clear diurnal trend in sub-15 μm particle mass in 6-hour samples from the St. Louis Regional Air Pollution Study (RAPS). Stevens et al. (1980) have found slightly higher daytime levels of sub-15 μm particle mass in a remote site in the Smoky Mountains; however, Pierson et al. (1980) noted no significant diurnal pattern in a forested region in Pennsylvania.

It is likely that day-night patterns are somewhat obscured by averaging times. Heisler et al. (1980) found peaks in light scattering and in particle mass corresponding to rush hours in Denver in the winter of 1978; minimum values were found in mid afternoon corresponding with mixing height maxima.

5.3.4.2 Weekly Patterns--Since human activity follows distinct weekly cycles, it is reasonable that anthropogenic sources of particles will also have weekly patterns. The most distinct weekly patterns are weekdays versus weekends. Trijonis et al. (1980) examined the St. Louis TSP and dichotomous data base for weekend-weekday differences in particle loadings. They concluded that there was only a slight (-9 percent) difference between weekend TSP values and weekday values for the average of five urban sites in St. Louis. For three suburban sites, the difference was -5 percent and for two rural sites the difference was -12 percent.

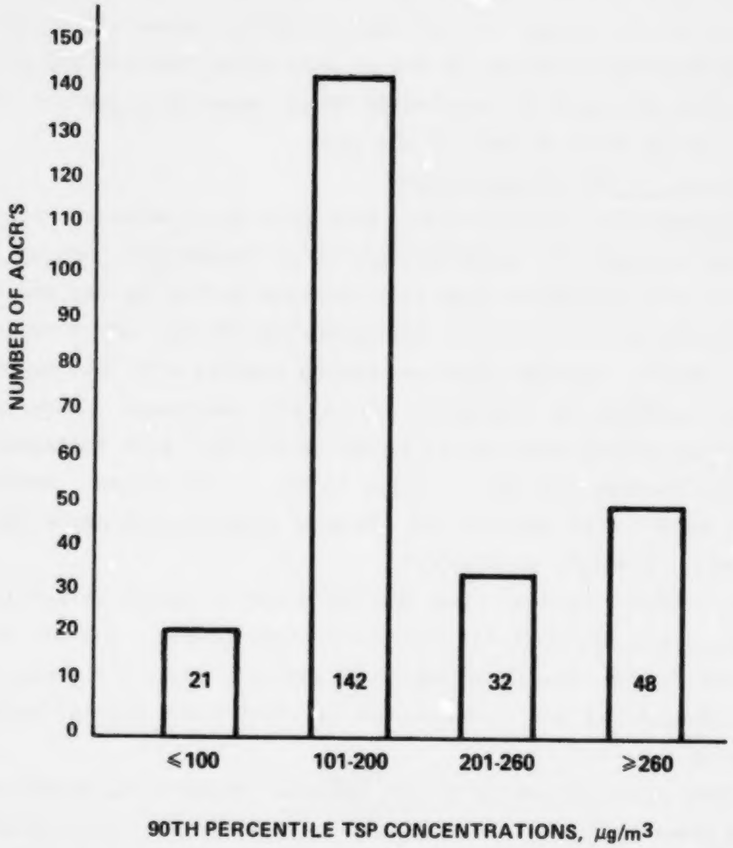

Figure 5-16. Severity of TSP peak exposures is shown on the basis of the 90th percentile concentration. Four ACQR's did not report.

Source: Environmental Protection Agency (1978).

The urban difference was dominated by readings from one monitor in a heavily industrial and commercial area.

5.3.4.3 Seasonal Patterns--Analyzing temporal patterns can frequently provide insight into the nature and source of PM. Meteorological parameters affect the generation and dispersion of particles. These parameters include (among others) degree-days, mixing height, ventilation factors, frequency of calms and stagnations, and precipitation. There are also seasonal patterns in some source emissions.

Because meteorological parameters are so important, it is likely that seasonal patterns in one area cannot be generalized to other areas. Trijonis et al. (1980) found a modest seasonal pattern of higher TSP concentrations in the summer months in St. Louis. In support of this observation, Figure 5-17 compares the TSP monthly mean values and the data from dichotomous samplers. The really distinct seasonal pattern was in the fine aerosol fraction. Summer fine-particle concentrations are twice as great as winter values. As discussed later, aerosol sulfates make up most of the fine-fraction particles and show a distinct seasonal pattern.

To illustrate the geographic specificity of these seasonal cycles, 3 years of monthly averaged TSP data are presented in Figure 5-18. The data came from Steubenville, OH, an industrialized site in the upper Ohio River Valley. Each monthly mean was derived from 20 or more sampling days. The TSP concentrations were considerably higher than the St. Louis values. The months with the highest TSP in Steubenville were March, April, and May in 1977; July, August, September, and November in 1978; and February and June in 1979. No clear seasonal pattern emerges from this 3-year period.

5.3.4.4 Yearly Trends--In 1957, a National Air Sampling Network (NASN) began to operate routinely on a national basis. The U.S. Public Health Service, with cooperation from State health departments, operated 231 urban and 37 nonurban stations. Some of these stations operated every other year, so in a given year there were 143 urban and 37 nonurban TSP hi-vol monitoring sites in operation. These sites collected one 24-hour sample every other week for a total of 26 samples per year. In 1977, over 4000 stations, most of them in State and local networks, reported TSP values to the National Aerometric Data Bank (NADB) of the U.S. EPA. Not only has the number of sites greatly increased, but the sampling frequency has been 1 day in 6 since 1971. In some cities, TSP monitoring data has been recorded for more than 20 years. Although the sites may not be in exactly the same locations for every city, general trends in TSP concentrations can be obtained. Figure 5-19 plots the annual geometric mean TSP concentrations for three groups of cities. In 1958, the five cities classified as industrial had annual mean TSP concentrations between 140 and 170 $\mu g/m^3$. By 1974 the annual mean concentrations had dropped to between 80 and 110 $\mu g/m^3$. Similarly, three of four cities classified as moderately industrialized showed substantial decreases. Only the Denver station recorded an increase, and that is only for a single year. The four cities classified as lightly industrialized showed less overall change.

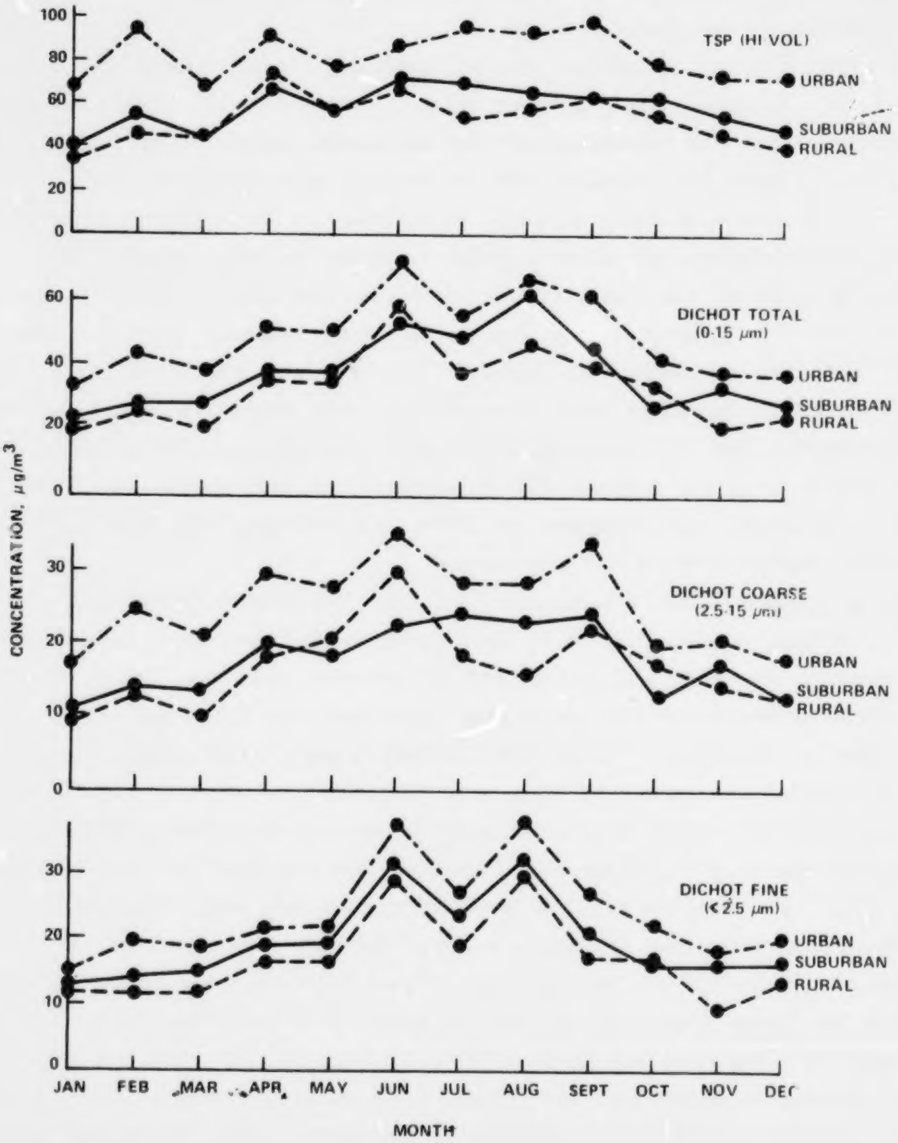

Figure 5-17. Seasonal variations in urban, suburban, and rural areas for four size ranges of particles. The data were obtained from a relatively small number of monitoring sites.

Source: After Trijonis et al. (1980).

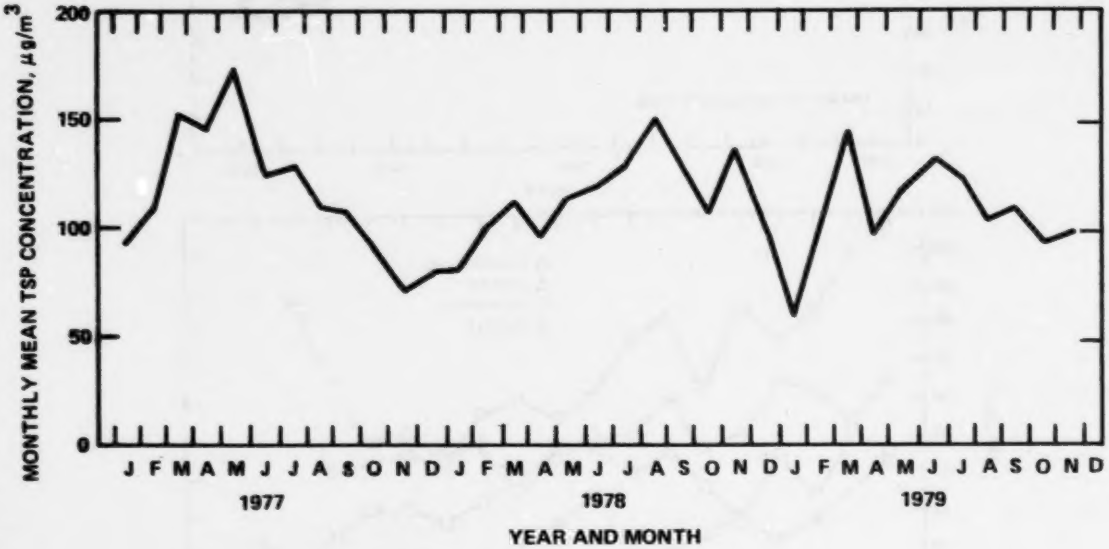

Figure 5-18. Monthly mean TSP concentrations are shown for the Northern Ohio Valley Air Monitoring Headquarters, Steubenville, OH. No clear seasonal pattern is apparent.

Source: Spengler (1980).

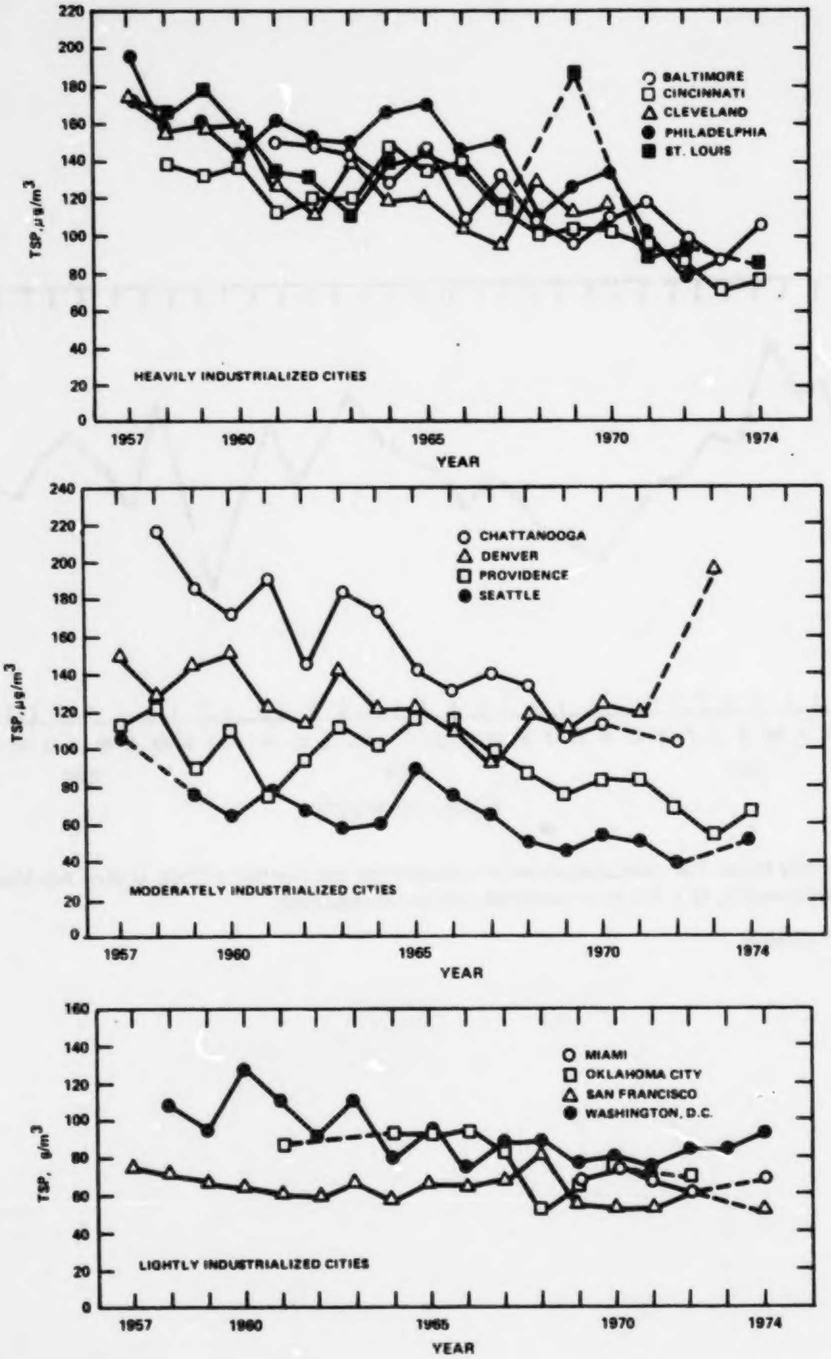

Figure 5-19. Annual geometric mean TSP trends are shown for selected NASN sites.

Source: U.S. Environmental Protection Agency (1978).

Examination of the expanded TSP data set from hi-vol samplers shows that for 2707 sites the composite median concentration has remained about 60 μg/m^3 between 1972 and 1977. The geometric mean over this period has decreased by approximately 8 percent. The decrease in the 90th percentile of the annual average concentrations is most pronounced over this period (see Figure 5-20). Lowering the TSP concentrations in locations with very high levels has been a target of State air pollution control strategies. In addition, relocating sources to rural regions, building new sources with taller stacks, converting to cleaner fuels, paving of streets and roads, and restricting open burning have decreased the number of locations experiencing annual concentrations of over 100 μg/m^3.

For the period 1970 to 1977, EPA reported an almost 50 percent reduction in particulate emissions. Most of this reduction occurred in the early 1970's as State air pollution control programs started many major emitters on compliance schedules. The rather modest composite overall reduction of 8 percent in annual TSP levels may be explained by the fact that direct emissions from stationary sources contribute only a fraction of the TSP loadings in the atmosphere.

Another perspective on regional differences is gained from observations of the 1978 data. Table 5-6 provides a statistical summary for the 50th and the 90th percentiles for valid monitors. Region IX ranked highest for the mean and maximum 50th and 90th percentiles, followed by Region VII, Region VI, and Region V. Regions I and II had consistently lower values.

The column presenting the standard deviations of the mean values for the 50th and 90th percentiles is also of interest. Smaller standard deviations suggest more uniformity in reported concentrations among monitoring sites. Because Regions I, II, and IV had less variance among sites than other regions, it could be interpreted that these regions had either more uniform distribution of pollution levels or more uniform placement of monitoring sites. The larger standard deviations in other regions, particularly in the West, probably mean that there is greater variation in pollution levels.

There are distinct regional differences in the trends of TSP concentrations. The distribution of site means and the actual rate of change in TSP levels differed among regions of the country. These trends are shown in Figures 5-21 and 5-22; the differences between years and even over the entire period were not tested for significance. Therefore, intraregion and interregion comparisons are presented qualitatively.

In the Eastern United States, in EPA Regions I and II, the composite average across sites decreased from 60 μg/m^3 to approximately 55 μg/m^3. The range of concentrations was much narrower in Regions I and II than it was in the more industrialized Regions III, IV, and V.

In Region III, the composite average decreased from 78 to 60 μg/m^3, with the 90th percentile in the distribution of annual mean concentrations decreasing from slightly over 100 μg/m^3 to about 90 μg/m^3. However, it has remained relatively stable or has even increased slightly since 1975. In Region V, the composite average decreased from 80 to 70 μg/m^3, and the 90th percentile decreased from 100 to 85 μg/m^3, reflecting the effectiveness of point source control.

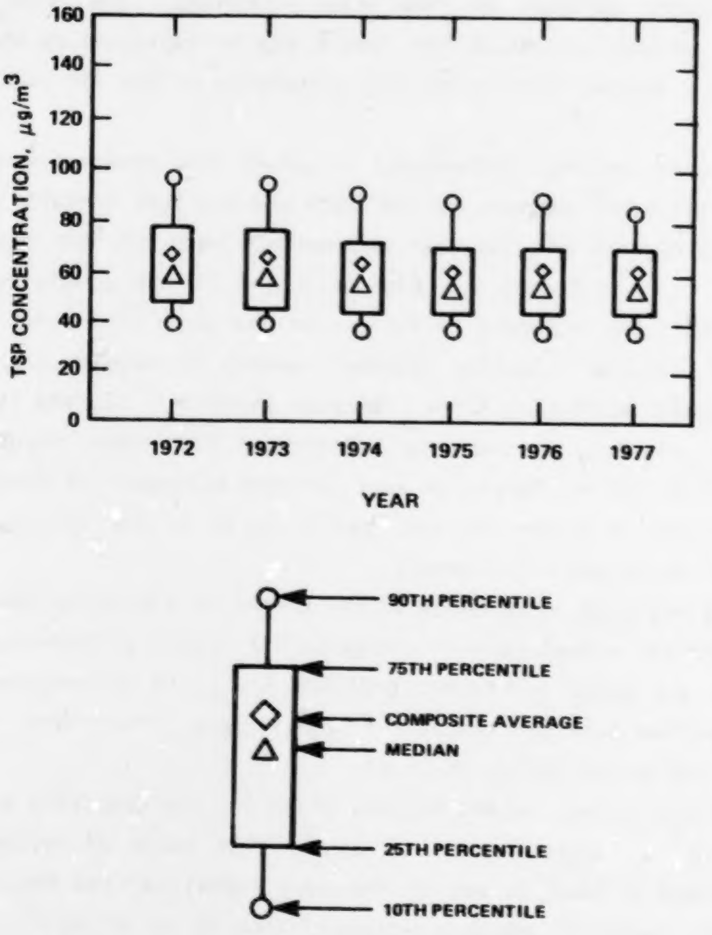

Figure 5-20. (Top) Nationwide trends in annual mean total suspended particulate concentrations from 1972 to 1977 are shown for 2707 sampling sites. (Bottom) Conventions for box plots.

Source: U.S. Environmental Protection Agency (1978).

TABLE 5-6. REGIONAL SUMMARIES OF TSP VALUES FROM VALID MONITORS

Number of sites	Region	Median				90th percentile			
		Minimum	Mean	Maximum	SD[a]	Minimum	Mean	Maximum	SD[a]
128	I	14.0	49.2	100.0	14.6	32.0	87.3	181.0	27.7
315	II	10.0	43.2	114.0	15.3	29.0	85.0	286.0	30.6
300	III	27.0	59.8	171.0	20.3	52.0	105.7	296.0	42.1
534	IV	22.0	55.3	137.0	17.2	41.0	93.5	256.0	30.9
781	V	13.0	64.1	189.0	22.0	26.0	122.4	383.0	42.8
294	VI	12.0	65.0	166.0	20.9	37.0	110.4	436.0	45.8
136	VII	34.0	69.7	154.0	20.2	58.0	123.6	359.0	44.2
152	VIII	7.0	54.8	164.0	32.8	18.0	107.8	412.0	64.0
89	IX	16.0	76.5	226.0	38.0	37.0	133.4	381.1	66.0
113	X	11.0	60.3	129.0	24.5	23.0	123.6	361.1	52.5
15	Alaska	11.0	48.1	94.0	22.7	35.0	137.1	250.0	68.7
9	Hawaii	25.0	39.7	70.0	13.7	40.0	63.6	99.0	18.9
10	Puerto Rico	32.0	54.3	85.0	13.9	66.0	90.7	134.0	18.9
2882	Total[b]	7.0	58.9	226.0	22.8	18.0	107.9	436.0	44.9

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[a] SD, Standard deviation of the median and 90th percentile values.
[b] Including American Samoa and Guam.

Source: SAROAD.

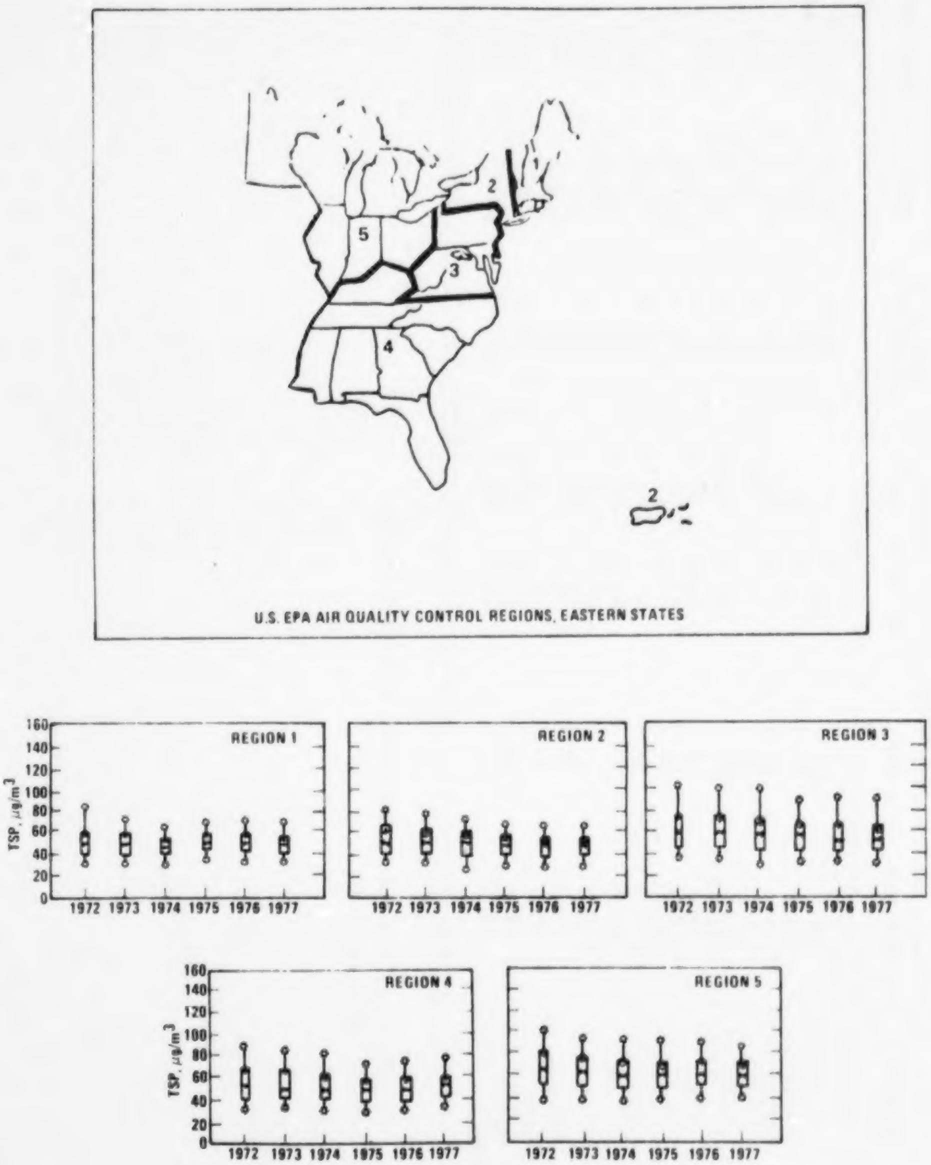


Figure 5-21. Regional trends of annual mean total suspended particulate concentrations, 1972-1977, Eastern states.

Source: U.S. Environmental Protection Agency (1978).

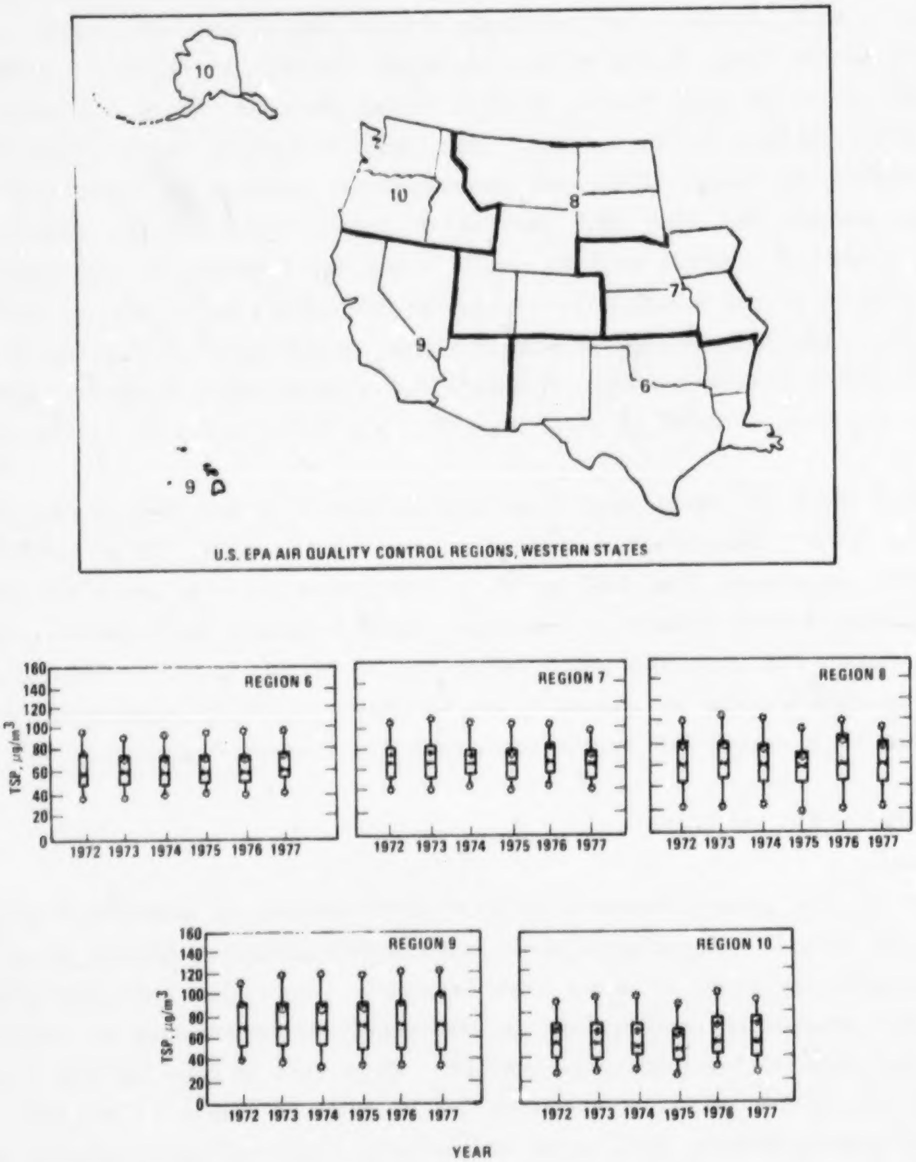


Figure 5-22. Regional trends of annual mean total suspended particulate concentrations, 1972-1977, Western states.

Source: U.S. Environmental Protection Agency (1978).

The Western States make up Regions VI through X. In Region VI, the composite average remained at approximately 75 μg/m^3, and the 90th percentile increased slightly from the 1973 reading to about 100 μg/m^3. Industrial, utility, and related growth in this area, as well as in Region IV, was probably responsible for keeping TSP concentrations from decreasing. In Region VII, the composite average was almost constant, varying only slightly between 80 and 75 μg/m^3. The 90th percentile varied between 110 and 100 μg/m^3. Region VIII showed wide distribution in the concentrations. The 10th percentile, at about 20 μg/m^3, was the lowest among all regions. The 90th percentile, approximately 100 μg/m^3, was roughly equal to the highest concentrations in most regions. The composite average varied over the 6-year record but remained essentially the same, approximately 80 μg/m^3, in 1977 as it was in 1972. The background air quality in the upper States of this region (Montana, North and South Dakota, and Wyoming) was among the best in the country. Thus, some of the low levels (20 μg/m^3 and below) represented some of the lowest background concentrations measured in the United States. The high composite average and high 90th percentile levels reflected the impact of locating monitors near industrial sources such as smelters and the fugitive dust emissions from windblown soils. Region IX had a composite average of 100 μg/m^3, which was up from 90 μg/m^3 in the early 1970's. The 90th percentile was also high, at 120 μg/m^3. Thus, Region IX had some of the highest levels in the country. Region X had a composite average of approximately 70 μg/m^3, up slightly from a low of 60 μg/m^3 in 1975. The 90th percentile varied between 90 and 100 μg/m^3.

The overall trend in improvement from 1972 through 1975 was followed by a reversal in some regions in 1976. Despite this short-term reversal in 1976, 60 percent of the sites showed long-term improvement from 1972 to 1977. For those sites at which TSP concentrations violated the current annual standard, 77 percent showed long-term improvements. Approximately 25 percent of these sites reported their lowest annual values in 1977. Possibly, the short-term reversal in 1976 was due to unusually dry weather, resulting in windblown dust that may have contributed to elevated TSP levels throughout the Central Plains, Far West, Southwest, and Southeast.

5.4 SIZE OF ATMOSPHERIC PARTICLES

5.4.1 Introduction

In Chapter 2, the general features of size distributions of atmospheric particles were discussed in some detail. In recapitulation, atmospheric particles tend to be more prevalent in certain particle size bands or modes than in others. Particles that have grown from the gas phase, either because of condensation or atmospheric transformation or combustion, occur initially as very fine nuclei 0.05 μm or smaller. These tend to grow rapidly to accumulation mode particles around 0.5 μm in size, which are relatively stable in the air. Because of their initially gaseous origin, this range of particle sizes includes inorganic ions such as SO_4^{2-}, NO_3^-, and NH_4^+, combustion-formed carbon, organic aerosols from photochemical conversions, and a variety of trace elements associated with combustion sources.

Airborne particles of soil or dust mostly result from entrainment by the motion of the air or from other mechanical action, and most of the mass of these materials is in particles larger than 5 μm. While the relative amounts of these two particle types are highly variable in both time and place, there is almost always a clearly observable minimum or gap in atmospheric mass distribution occurring in the particle size range of roughly 1 to 3 micrometers. In this range, there are only minor percentages of the total mass, and this material appears to be overlap from the two major categories. The larger particles frequently contain clay minerals, bits of local rocks, limestone aggregate from roadways, fly ash from power plants, and other substances ranging from insect parts, pollen, and sawdust to liquid globules of acidic smut blown from boiler tubes (Draftz and Severin, 1980). The elemental analysis of these larger particles is usually dominated by silicon, aluminum, magnesium, calcium, and iron, all components of soil and of fly ash (see Chapter 4).

In the last several years, a general perception has been growing that not all PM is equally damaging to the environment (see Chapters 8 & 11). For this reason. information on the mass of PM in various size categories has been gradually accumulating and is here summarized. Furthermore, a national network of sampling stations equipped with size-selective sampling devices is currently being set up. While some tabulated data are available from this network and are summarized here, no detailed interpretative analysis has been published yet, nor are any chemical analytical data available. The analysis of monitoring results from the national inhalable particle (IP) network must wait for subsequent revisions of this document.

In the following discussion, the major chemical components of atmospheric aerosols are organized by the size mode or particle category in which they are most frequently observed. This is not to say that SO_4^{2-} ion, for example, is exclusively a component of fine particles. Sometimes, e.g. in the vicinity of a cement manufacturing facility, there can be substantial amounts of coarse $CaSO_4^{2-}$. However, the relationship between size and composition of particles is so general that more reason is served by this organization than by any other.

Since the finer particles seem to have less diversity and since measurements of the major anion components of this fraction have been made for a long time, this group is discussed first. The more complicated coarse fraction has not been very well defined and, indeed, may not be definable by chemical analysis alone. There is considerable interest in this size range currently, though, and studies of these materials are cited in Section 5.6.

5.4.2 Size Distribution of Particle Mass

Evidence from chemical analysis and physical theory (Chapter 2) strongly suggests that atmospheric aerosols commonly occur in two distinct modes. The fine or accumulation mode is attributed to growth of particles from the gas phase and subsequent agglomeration. The coarse mode is made up of mechanically abraded or ground particles. Therefore, it is not surprising to find atmospheric PM distributed among fine and coarse particles with a rather clear interval of demarcation in between.

Unfortunately, gravimetric data by size fraction were sparse until comparatively recently. Furthermore, most were obtained with impactors, which are influenced by particle "bounce" (see Chapter 3). Several works suggested the existence of a distinct minimum in the mass-size distribution in the 1968 to 1970 time period. Lee et al. (1968) observed only 14-percent of the aerosol mass between 2 and 4 μm in three samples from Fairfax, OH. Lundgren (1970) found only 10-percent of aerosol mass in this range in 10 Riverside, CA, aerosols samples ranging from 47 to 144 $\mu g/m^3$. O'Donnell et al. (1970) found only 10-percent in the 2 to 4 μm range in one Pittsburgh, PA, sample. Lee and Goranson (1972) and Lee et al. (1972) reported many impactor size distributions for six cities obtained in 1970, all indicating 12- to 15-percent of aerosol mass between 2 to 5 μm. However, many of these data were clouded by bounce and entry losses and probably were biased toward low coarse-mode distributions.

More recently, evidence from electrostatic sizing equipment has confirmed this general trend. Figures 5-23 through 5-26 show the distribution of particle volume by size. These data differ from mass distributions because particle density (mass/volume) was not measured as a function of size. Figures 5-23 and 5-24 present distributions in and around St. Louis, MO, for a variety of conditions. Generally these distributions show distinct minimum values in the vicinity of 1 to 2 μm.

However, the combined influence of nearby sources and aerosol aging can produce major shifts in volume and, presumably, mass distribution. For example, Figure 5-24 shows a third, very fine "nuclei" mode of particles centering around 0.05 μm. This mode can be attributed to the presence of nearby automotive traffic. Also shown in Figure 5-24 is the rather narrow size distribution from a coal-fired power plant adding to the fine aerosol burden. However, the mass-size distribution from large sources can vary dramatically among sources depending on the type and efficiency of control equipment (see Chapter 4).

There can be major shifts in the relative proportions of fine and coarse particle mass as an aerosol ages (i.e., moves with the wind). Figures 5-25 and 5-26 show dramatic examples of this phenomenon obtained during the 1972 California Aerosol Characterization Experiment (ACHEX). In the first case, aged aerosol was transported in the wind to the site from the Los Angeles area; during this process coarse particles settled out. In the second case, local winds stirred up dust, shifting the distribution toward larger sizes (Whitby, 1980).

A summary of mass data calculated from electrostatic size distributions for several environments is shown in Table 5-7. Here, the dramatic variations in coarse and fine particle fractions found in practice are clear.

More recently, a number of studies have been done with dichotomous samplers designed to obtain mass samples of the 0 to 2.5 μm fine fraction and a 2.5 to 15 μm coarse fraction. Researchers from EPA's Environmental Science Research Laboratory have measured coarse and fine aerosol mass concentrations in several locations: Dzubay et al. (1977) report on 18 days of

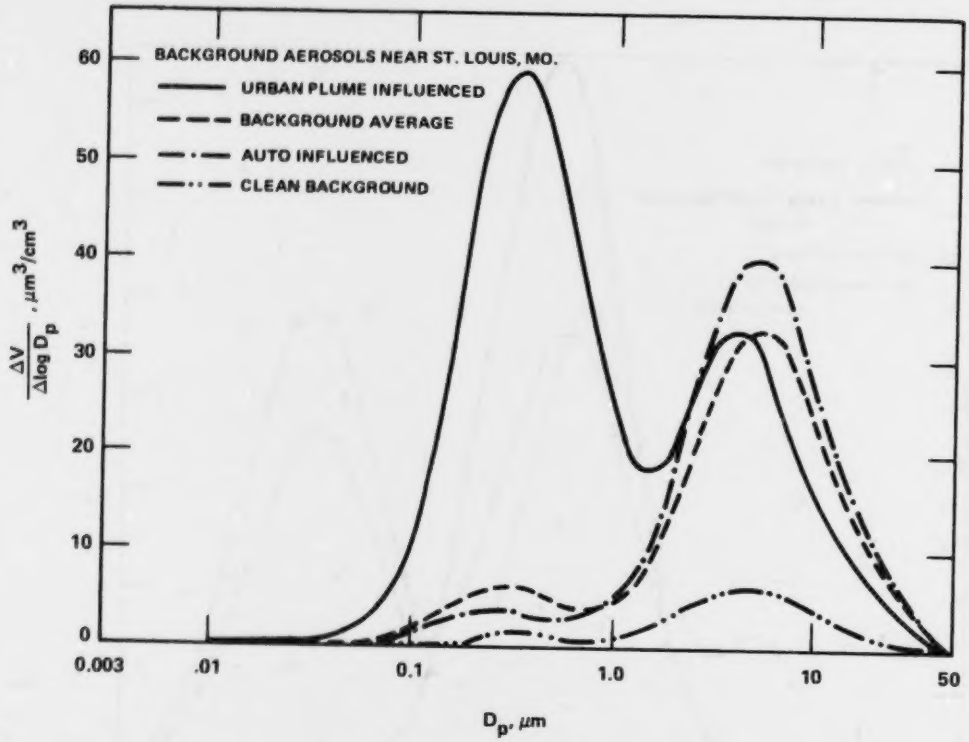


Figure 5-23. Linear-log plot of the volume distributions for the four background distributions. Notice how much the urban plume adds to the accumulation mode of the background.

Source: Cantrell and Whitby (1978).

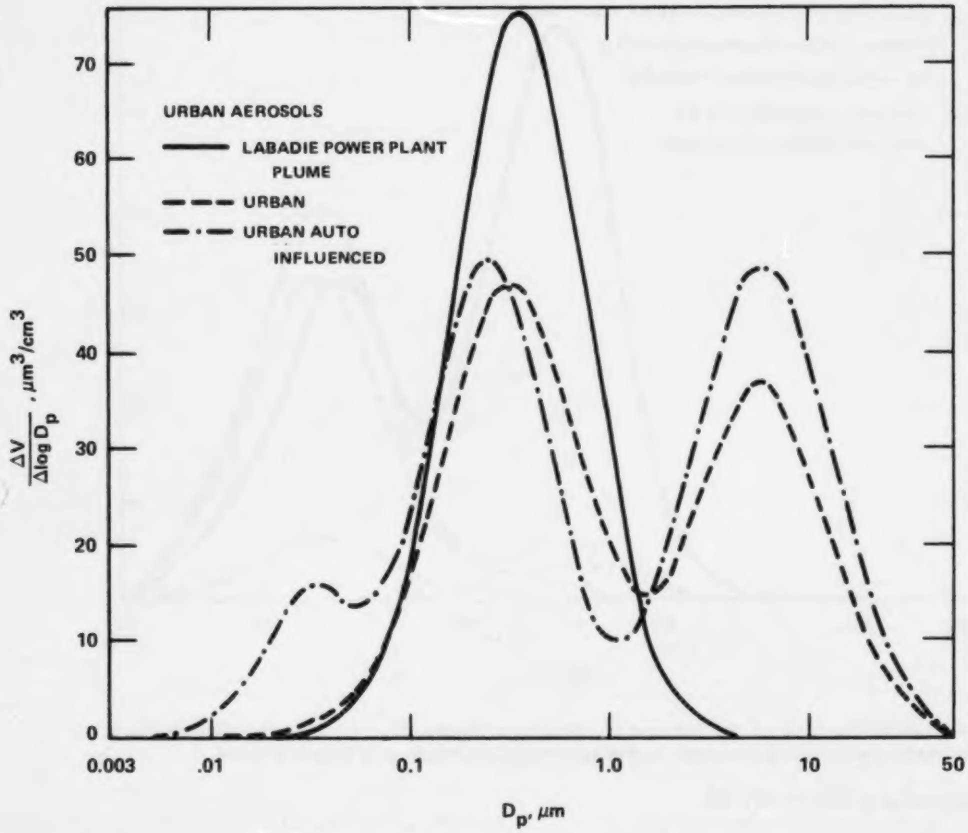


Figure 5-24. Linear-log plot of the volume distributions for two urban aerosols and a typical distribution measured in the Labadie coal-fired power plant plume near St. Louis. Size distributions measured above a few hundred meters above the ground generally have a rather small coarse particle mode.

Source: Cantrell and Whitby (1978).

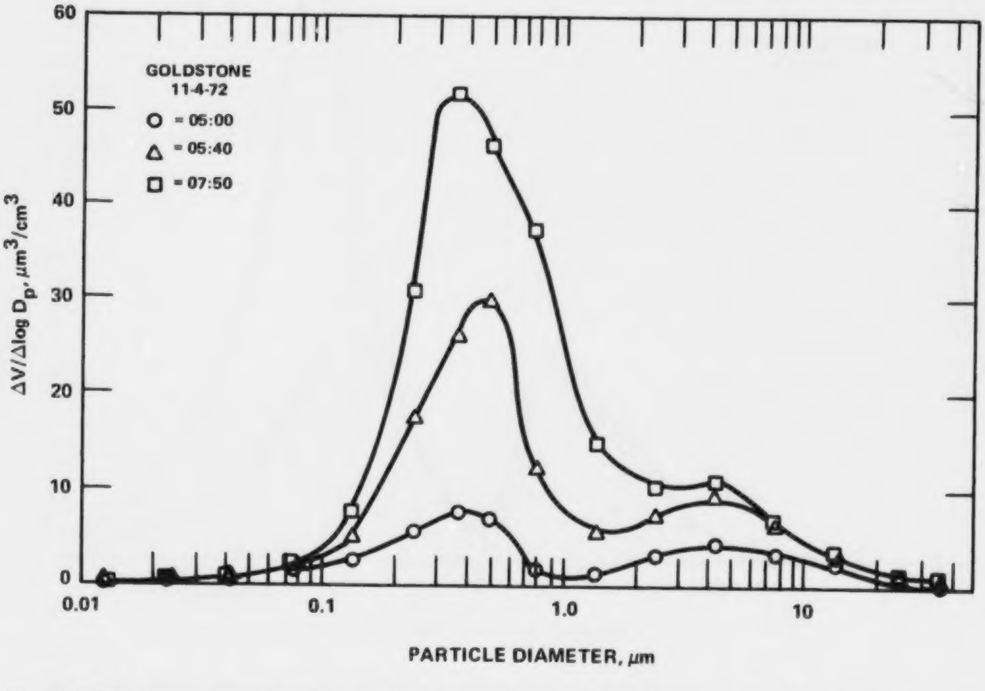


Figure 5-25. Incursion of aged smog from Los Angeles at the Goldstone tracking station in the Mojave Desert in California. Note the buildup in the accumulation mode.

Source: Whitby (1980).

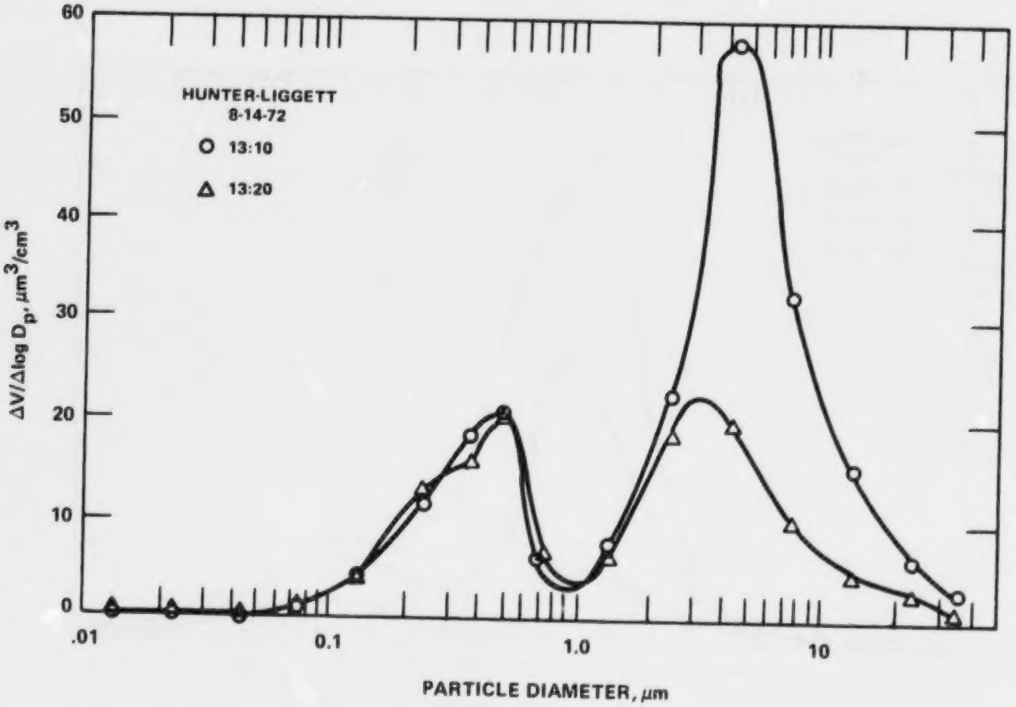


Figure 5-26. Sudden growth of the coarse particle mode due to local dust sources measured at the Hunter-Liggett Military Reservation in California. This shows the independence of the accumulation and coarse particle mode.

Source: Whitby (1980).

TABLE 5-7. FINE AND COARSE AEROSOL CONCENTRATIONS FROM SOME URBAN MEASUREMENTS COMPARED TO CLEAN AREAS

Location	Condition	Concentration (μg/m^3)[a]	
		Fine particles	Coarse particles
St. Louis	Very polluted	296.0	94.0
Los Angeles	Grand average	37.0	30.0
Los Angeles freeway	Wind from freeway	77.0	59.0
Denver	Grand average	16.6	23.2
Goldstone	Clean	1.5	3.0
Milford, Mich.	Very clean	1.03	0.82
Pt. Arguello (seaside)	Marine air	1.1	53.0

[a] Calculated from volume distribution using assumed particle density, $\rho p = 1$ gm/cm^3.

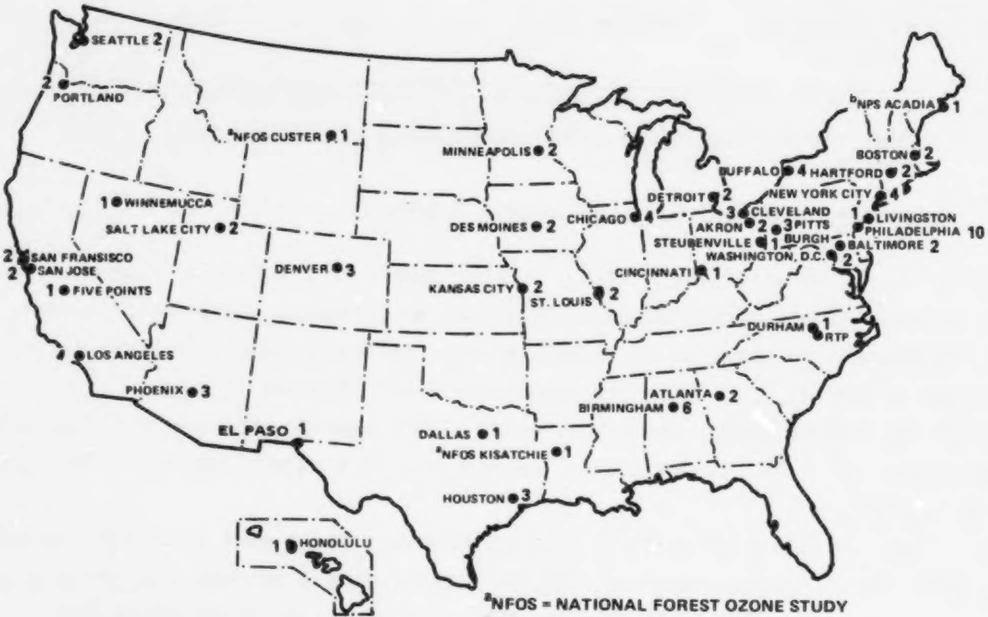
Source: National Research Council (1979).

summer sampling in St. Louis; Stevens et al. (1979) report on 2 months of summer sampling in Houston, TX; Stevens et al. (1980) discuss results of an extensive sampling for a week in the Great Smoky Mountains. Courtney et al. (1980) discuss the early results from winter sampling at two locations in Denver, CO. Table 5-8 summarizes their reported findings.

In another short-term study, Lewis and Macias (1980) sampled atmospheric aerosols for 21 days in Charleston, WV. The fine-fraction average was 33.4 μg/m^3, and the coarse fraction average was 27.1 μg/m^3.

Because of the influence of particle size on adverse effects such as health, visibility, and soiling (see later effects chapters), EPA is establishing a network of size-selective PM monitors. Ultimately this grid will include 250 stations to be established over a 3-year period. During the period from April 1, 1979, to June 30, 1980, 94 stations were established. A map showing current sampler locations is shown in Figure 5-27 (U.S. Environmental Protection Agency, 1981). Since dichotomous samplers are used in this network, together with hi-vols, it is possible to obtain a general conception of the relationship between TSP (0 $^{\tau}$ ~ 60 μm), dichotomous total or "inhalable" particle mass (0-15 μm), and the fine and coarse fractions defined above.

A total of 1960 dichotomous fine- and coarse-mass measurements and 2675 TSP measurements are now in this data base; hi-vol measurements with a size-selective inlet are now also being made. In this data base, daily TSP values range from 33.2 μg/m^3 in Litchfield, CT to 474.4


SEATTLE 2
2 PORTLAND
aNFOS CUSTER 1
MINNEAPOLIS 2
bNPS ACADIA 1
BOSTON 2
BUFFALO 4
HARTFORD 2
1 WINNEMUCCA
DETROIT 2
NEW YORK CITY 4
SALT LAKE CITY 2
DES MOINES 2
CHICAGO 4
3 CLEVELAND
AKRON 2
3 PITTSBURGH
1 LIVINGSTON
PHILADELPHIA 10
STEUBENVILLE 1
BALTIMORE 2
2 SAN FRANSISCO
2 SAN JOSE
DENVER 3
WASHINGTON, D.C. 2
CINCINNATI 1
1 FIVE POINTS
KANSAS CITY 2
ST. LOUIS 2
DURHAM 1
RTP 2
4 LOS ANGELES
PHOENIX 3
ATLANTA 2
BIRMINGHAM 6
EL PASO 1
DALLAS 1
aNFOS KISATCHIE 1
HOUSTON 3
1 HONOLULU

[a]NFOS = NATIONAL FOREST OZONE STUDY
[b]NPS = NATIONAL PARK SERVICE
SMALL NUMBERS REPRESENT NUMBER OF SAMPLING SITES AT EACH LOCATION

Figure 5-27. Inhalable-particle network sites established as of March 19, 1980.

Source: U.S. Environmental Protection Agency (1981).

TABLE 5-8. FINE FRACTION AND COARSE FRACTION DICHOTOMOUS SAMPLING BY ENVIRONMENTAL SCIENCE RESEARCH LAB, USEPA IN FOUR LOCATIONS

Location	Period	Days	Comments	Concentration Fine (μg/m³)	Coarse (μg/m³)
St. Louis	Summer	18	Urban	29	22
			Rural	26	15
Houston	Summer	28	Urban	52.2	39.8
Denver	Winter	19	Urban Site D	18.1	22.5
			Urban Site N	25.4	23.4
			Urban Site D	23.2	33.0
			Urban Site N	26.4	26.5
	Winter	19	Urban	26.5	27.1
	Spring	28	Urban	16.1	9.8
Smoky Mtns	Fall	7	Remote Day	26.4	6.2
			Remote Night	22.0	4.9

Source: Courtney et al. (1980)

to 474.4 μg/m^3 in Dallas, TX. Maximum dichotomous sampler totals (fine + coarse) ranged from 28.7 μg/m^3 in Pearl City, HI, to 267.5 μg/m^3 in Rubidoux, CA (U.S. Environmental Protection Agency, 1981).

Because of the limited time period available for analysis (April 1979 to June 1980), it would be unwise to consider analysis of these data as indicative of geographical or seasonal trends in particle size. But some additional general factors associated with particle size can be seen from inspection of the data summary in Table 5-9. (The ratios in the table are averages of ratios of individual sample pairs and thus will not equal ratios of the average concentrations given.)

On the average the dichotomous sampler total mass was about 67 percent of the TSP (Pace, 1980), but this ratio varied widely across the country, from about 0.4 to almost 1 in Portland, OR and Litchfield, CT (five samples). However, most Portland and all Litchfield samples were collected during the winter months when rainfall or snow cover could have materially reduced dust levels.

The fraction of fine and coarse components was even more variable. The coarse mass fraction of the total sub-15 μm mass ranged from about one-fifth to two-thirds in this selected set and was even higher for individual days. Particularly striking were the average values for Dallas and El Paso, TX. At both sites, the sub-15 μm mass was only about half the TSP mass. However, in Dallas only 27 percent of this was in the 2.5 to 15 μm range while in El Paso, 64 percent was "coarse."

TABLE 5-9. RECENT DICHOTOMOUS SAMPLER AND TSP DATA FROM SELECTED SITES--ARITHMETIC AVERAGES

Location		No. of observations	TSP $\mu g/m^3$	D_{TOTAL}/TSP (# pairs)	Coarse $\mu g/m^3$	Fine $\mu g/m^3$	Coarse/ D_{TOTAL}
Northeast							
Buffalo, NY	TSP	28	93.7	0.70 (21)	25.2	25.9	0.50
	D_{Total}	40					
Erie Co., NY	TSP	41	32.8	0.64 (25)	5.1	16.2	0.24
	D_{Total}	44					
Litchfield, CN	TSP	5	18.9	0.86 (1)	6.6	13.3	0.33
	D_{Total}	5					
Philadelphia, PA	TSP	102	45.1	0.83 (40)	13.3	22. 5	0.38
	D_{Total}	109					
Southeast							
Birmingham, AL	TSP	38	60.8	0.68 (23)	15.0	24.4	0.38
	D_{Total}	40					
Midwest							
Minneapolis, MN	TSP	44	50.1	0.61 (26)	15.6	16.4	0.46
	D_{Total}	41					
Cincinnati, OH	TSP	51	53.6	0.77 (26)	14.4	25.2	0.35
	D_{Total}	48					
Southwest							
Dallas, TX	TSP	22	94.9	0.47 (21)	9.8	24.1	0.27
	D_{Total}	24					
El Paso, TX	TSP	29	86.5	0.51 (7)	46.3	11.7	0.64
	D_{Total}	26					
Far West							
Los Angeles, CA	TSP	43	68.4	0.53 (18)	21.3	24.6	0.47
	D_{Total}	50					
Portland, OR	TSP	37	66.7	0.90 (19)	42.3	22.0	0.60
	D_{Total}	36					
Pearl City, HA	TSP	27	33.0	0.43 (11)	7.9	8.4	0.47
	D_{Total}	25					

Source: U.S. Environmental Protection Agency (1981).

Pace et al. (1981) analyzed some of the general features of these preliminary IP network data. These authors concluded that regional scale fine particle mass ranged from 6 to 13 $\mu g/m^3$ in the Western States and from 15 to 23 $\mu g/m^3$ in the eastern United States, comparing only four sites in each category. They also found strong influence of local sources around monitors in urban sites. "Concentration changes averaging 16 $\mu g/m^3$ or 31 percent were found in sites separated by as little as 1 km distance," according to this study. No strong seasonal trends were found in various regions of the United States, although there appeared to be slightly higher fine-particle mass in the summer than in spring in the eastern United States.

It appears that chemical analysis and several years more data from the IP network could considerably increase understanding of temporal and spatial distribution of fine- and coarse-particle fractions.

5.5 FINE PARTICLES IN AIR

Sulfate, ammonium ions, organics, carbon, and combustion-associated metals are widely recognized to be the major components of fine PM. Few studies of aerosol composition have attempted material balance, and fewer still have done so with size fractionation.

Nevertheless, a great deal has been learned about the chemical and elemental composition of airborne particles since the early experiments in the 1950's by Junge in Germany, Massachusetts, Hawaii, and various sites in Florida (Junge 1952). Junge's observation that sulfate and ammonium ions appear predominantly in the fine-particle fraction has been confirmed in independent field observations, both in urban and rural areas (Lewis and Macias, 1980; Dzubay and Stevens, 1975). In analyzing the St. Louis, MO, dichotomous sampler data by x-ray fluorescence, Dzubay found 75 percent of the zinc, sulfur, bromine, arsenic, selenium, and lead occurred in the fine particles and at least 75 percent of the silicon, calcium, titanium, and iron in the coarse fraction (Dzubay, 1980).

In studies of Charleston, WV, particles, Lewis and Macias (1980) reported material balances of fine and coarse particles accounting for 69 percent and 60 percent of the mass, respectively. Eighty-five percent of the sulfate and ammonium ions were in the fine particles where they accounted for 30 and 12.8 percent of the mass, respectively. Carbon, both elemental and organic, was mainly in the fine aerosol (61 percent) where it accounted for 18.2 percent of the mass.

Stevens et al. (1978) reviewed size-fraction analyses for St. Louis, MO and Charleston, WV and for four other sites including New York, NY; Portland, OR; Philadelphia, PA; and Glendora, CA. They conclude that sulfate ion is predominantly a fine component (70 percent) that usually accounts for 40 percent of the mass of that fraction and occasionally up to 50 percent. The SO_4^{2-} must be present as ammonium salts or as H_2SO_4 since metallic sulfate could be only 10 to 30 percent of the total at maximum (Stevens et al., 1978).

In one site in the Great Smoky Mountains, 89 percent of the fine PM was identified (Stevens et al., 1980). Sulfate accounted for 61 percent; ammonium ion, 12 percent; elemental carbon, 5 percent; and organic carbon, 10 percent. Trace elements, mainly lead, made up the balance. In this study, only organic carbon was also a significant component of the coarse particles.

Studies in a number of sites in California produced similar results. Flocchini et al. (1978) and Cahill et al. (1977) reported size-fraction distributions for sulfur (presumably SO_4^{2-}) in three districts of California. In all areas, sulfur was present almost exclusively in the sub-3.6 µm fraction. In dry weather, sulfur was found in sub-0.65 µm fractions, while under humid conditions it appeared in the 0.65 to 3.6 µm cut.

Since SO_4^{2-}, NH_4^+, elemental carbon, and organics are the major components of the fine aerosol, analytical data relating thereto, whether size fractionated or total, will be discussed together in this section.

5.5.1 Sulfates

The term "atmospheric sulfates" describes a several sulfur compounds, including ammonium sulfate, NH_4HSO_4, H_2SO_4, letovicite, calcium sulfate, and a variety of metal salts. Most of the historic data on atmospheric concentrations of sulfates are based on the water-soluble extract of TSP filters and measurements of the sulfate ion. These samples were subject to artifact formation on the glass fiber filters used in the early NASN measurements. For a complete discussion of these issues, see Chapter 3. It is now generally accepted that TSP SO_4^{2-} measurements taken before 1974 or 1975 using the traditional glass fiber filters may have overestimated sulfates by as much as 2 µg/m^3 or more in areas where ambient SO_2 concentrations were high.

Annual average TSP SO_4^{2-} concentrations range from less than 1 µg/m^3 in some States to almost 20 µg/m^3 in urban industrial areas of the Northeast. For 24-hour average concentrations, SO_4^{2-} concentrations range from near zero to more than 80 µg/m^3.

Sulfate, particularly ammonium sulfate, appears to account for the majority of fine PM in many locations (Dzubay, 1980; Stevens et al., 1980; Watson, 1979; Flocchini et al., 1978; Stevens et al., 1978; Pierson et al., 1980). Although some of this material may be emitted directly from sources, the majority appears to be secondary (i.e., formed by chemical reactions in the atmosphere) (Friedlander, 1973; Grosjean and Friedlander, 1975).

5.5.1.1 Spatial and Temporal Variations--The spatial distribution of measured SO_4^{2-} concentrations for 1974 is displayed in Figure 5-28. Figure 5-28(a) presents the annual average concentrations. An area having an annual average of more than 15 µg/m^3 extended from the lower Ohio Valley through the upper Ohio Valley, including major portions of Kentucky, West Virginia, Ohio, and western Pennsylvania. The areas with annual averages exceeding 10 µg/m^3 included almost all of the United States east of the Mississippi, except for the South Atlantic States and upper New England.

Through the Central Midwest area, values of 4 to 9 µg/m^3 were reported. The Far West States and the Pacific Northwest experienced annual SO_4^{2-} levels below 2 to 3 µg/m^3, except for the Los Angeles area. The Los Angeles levels are not shown in this figure, but a 1975 National Academy of sciences report on air quality and stationary source emission controls indicated that they were between 7 and 13 µg/m^3 (National Academy of Sciences, 1975).

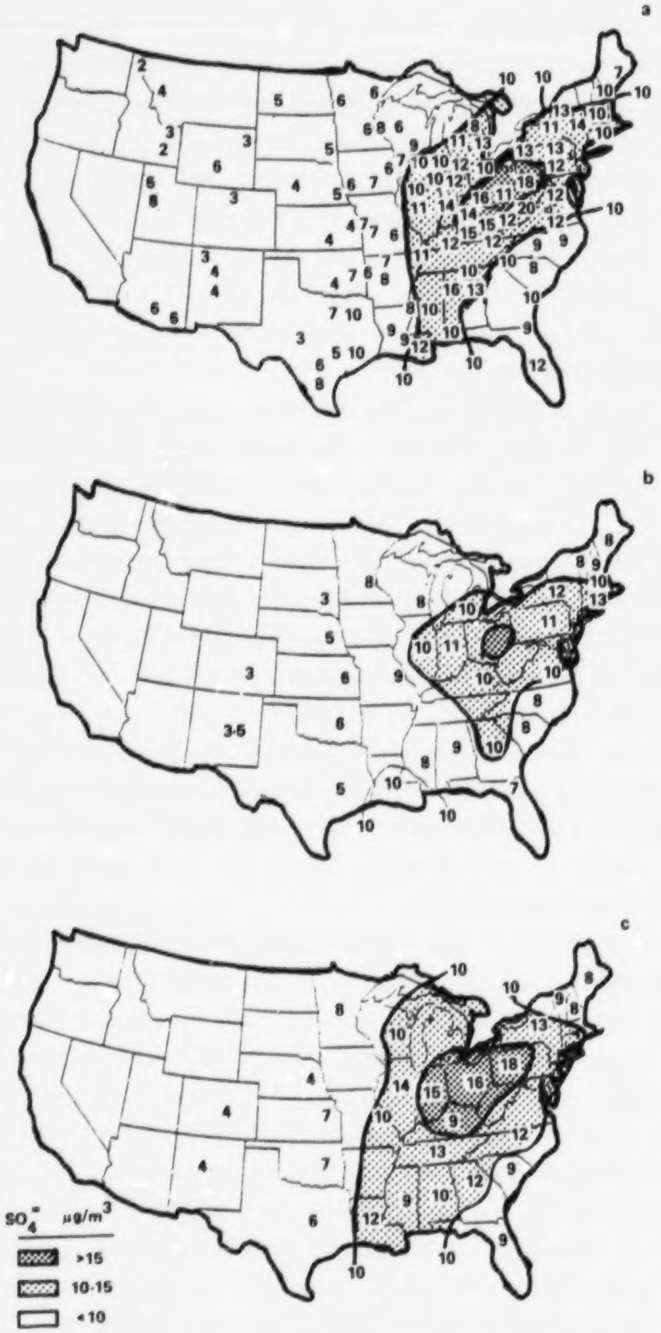

a
b
c
$SO_4^=$ µg/m^3
>15
10-15
<10

Figure 5-28. Contour maps of sulfate concentrations for 1974 are shown for: (a) annual average; (b) winter average; (c) summer average.

Source: National Research Council (1978a).

Seasonal variations in SO_4^{2-} concentrations are shown in Figures 5-28(b) and 5-28(c) for the winter months and the summer months respectively. The area of elevated SO_4^{2-} greatly expands during the summer months. As demonstrated by several regional studies on atmospheric SO_4^{2-} transport, SO_4^{2-} concentrations can be elevated over large geographical regions under certain meteorological conditions (Eliassen, 1978; Lyons and et al., 1978; Perhac, 1978; Whelpdale, 1978). This supports the idea of transport and conversion beyond the source regions of SO_2 emissions. As these contour maps clearly show, a sizeable portion of the U.S. population is exposed to annual SO_4^{2-} concentrations of more than 10 μ/m^3 in the ambient air. In view of the rising SO_2 emissions from increased use of coal throughout the United States, particularly in the South Central States, the area of maximum SO_4^{2-} levels might expand and shift to the lower Ohio Valley and the Southeast.

In a large-scale study of atmospheric SO_4^{2-} in eastern Canada, Whelpdale (1978) reported mean levels of 10 $\mu g/m^3$ over southern Ontario. The mean levels of sulfates dropped to less than 2.5 $\mu g/m^3$ above the 49th parallel. Figure 5-29 displays these values for the period of study. During episodic conditions primarily affecting the lower Great Lakes region, 24-hour concentrations were reported as high as 40 to 50 $\mu g/m^3$. Such episodic conditions are associated with a high-pressure cell over eastern Canada with southwest flow occurring on the back side of the high pressure. This synoptic situation favors transport of SO_2 and sulfates from the high SO_2 source regions of the industrialized northeastern United States.

Recently, new information on the interrelationship of SO_2, NO_2, O_3, TSP, sulfates, and nitrates has become available from a large-scale regional study. The Electric Power Research Institute (EPRI) Sulfate Regional Experiment (SURE) involves intensive monitoring from some 54 rural stations and an aircraft sampling program. The area being studied is 2400 by 1840 kilometers; it extends from Kansas to the Atlantic coast and from mid-Alabama to southeastern Canada (Hidy et al., 1979) (see Figure 5-30).

Mueller et al. (1979) reported on the earlier SURE data collected in 1974 and 1975 and presented the preliminary results of an intensive field study made during July 1977 through February 1978. Using the limited historical data base, they indicated that the rural stations experienced a frequency of occurrence of 24-hour average SO_4^{2-} concentration similar to that observed around large metropolitan areas such as New York City. As seen in Figure 5-31, 24-hour values greater than 10 $\mu g/m^3$ occurred in approximately half the data, and the occurrence of 24-hour SO_4^{2-} levels exceeding 20 $\mu g/m^3$ was about 10 to 12 percent.

Based on concentrations of 10 to 20 $\mu g/m^3$ as an indicator of elevated exposure, the average concentrations over the entire SURE network area were estimated by a linear interpolation procedure with a resolution of 80 by 80-km grids. Episodes of elevated sulfates were extensive; during an episode in early August 1977, the area where SO_4^{2-} levels exceeded 20 $\mu g/m^3$ expanded to more than 500,000 km^2. Two regional episodes occurred in January and early February 1977. In August, 39 percent of the SO_4^{2-} values exceeded 10 $\mu g/m^3$; in January the figure was 30 percent. Five percent of the values exceeded 20 $\mu g/m^3$. In October, 20 percent of the values exceeded 10 $\mu g/m^3$, and less than 1 percent of the values exceeded 20 $\mu g/m^3$.

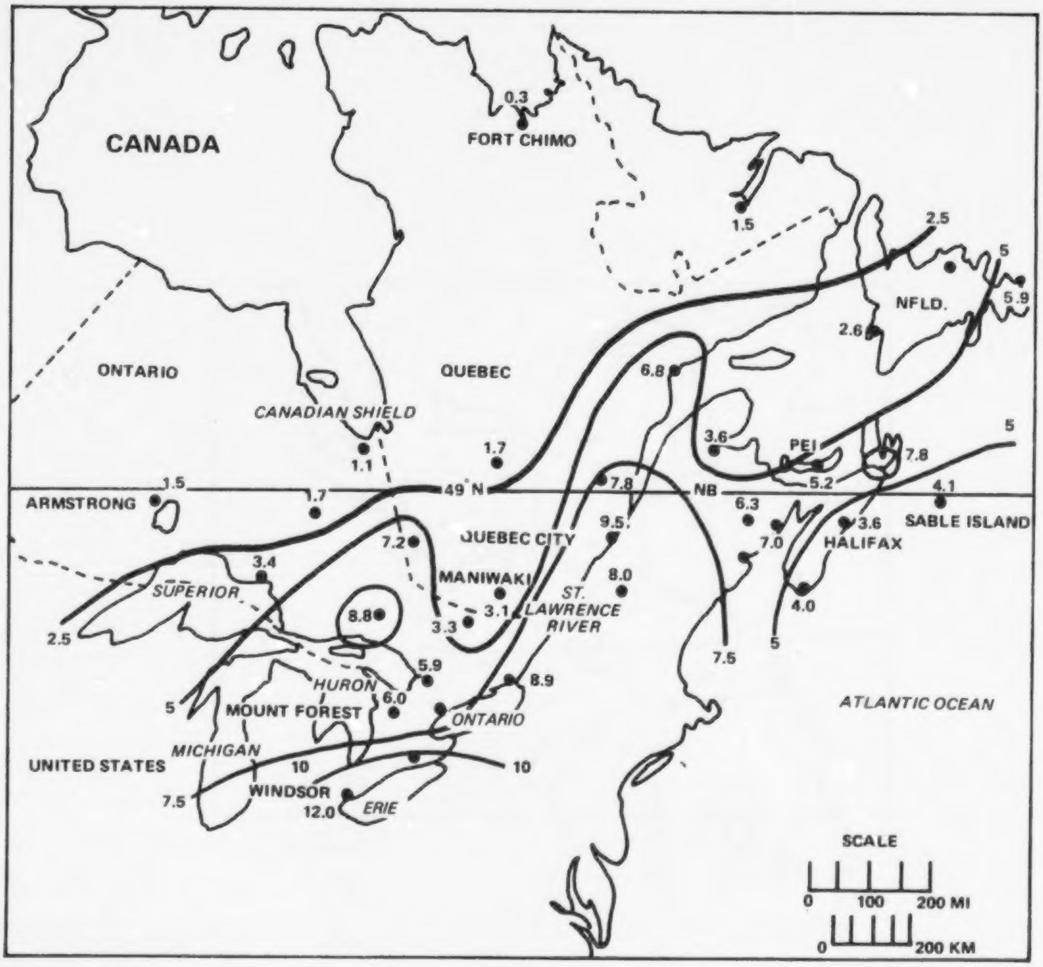

CANADA
0.3
FORT CHIMO
1.5
2.5
5
5.9
NFLD.
2.6
ONTARIO
QUEBEC
6.8
CANADIAN SHIELD
1.1
1.7
3.6
PEI
7.8
5
1.5
ARMSTRONG
1.7
49° N
7.8
NB
5.2
4.1
6.3
3.6
SABLE ISLAND
9.5
7.2
QUEBEC CITY
7.0
HALIFAX
3.4
SUPERIOR
MANIWAKI
8.0
ST. LAWRENCE RIVER
3.1
3.3
8.8
2.5
4.0
7.5
5
5.9
HURON
8.9
5
MOUNT FOREST
6.0
ONTARIO
ATLANTIC OCEAN
MICHIGAN
UNITED STATES
10
10
WINDSOR
7.5
12.0
ERIE
SCALE
0
100
200 MI
0
200 KM

Figure 5-29. Intensive Sulfate Study area in Eastern Canada shows the geometric mean of the concentration of soluble particulate sulfate during the study period. Units are micrograms of sulfate per cubic meter.

Source: Whelpdale (1978).

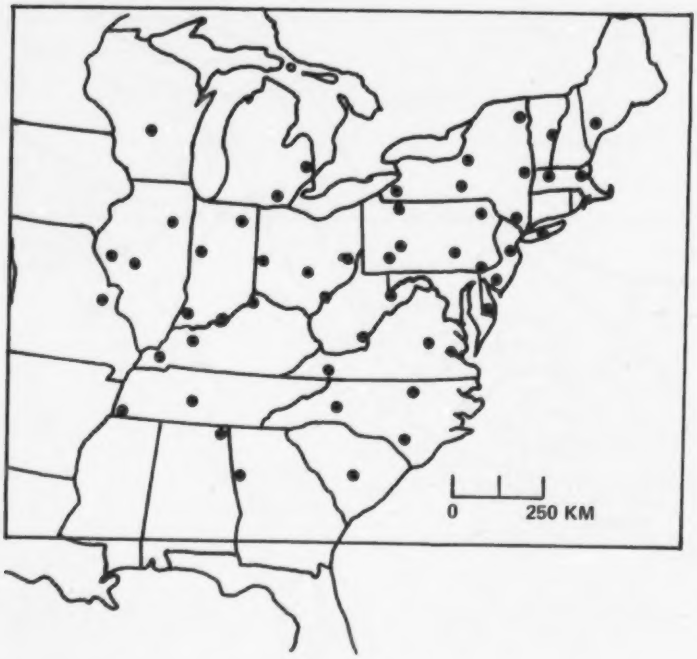


Figure 5-30. Map of SURE region shows locations of ground measurement stations.

Source: Hidy et al. (1979).

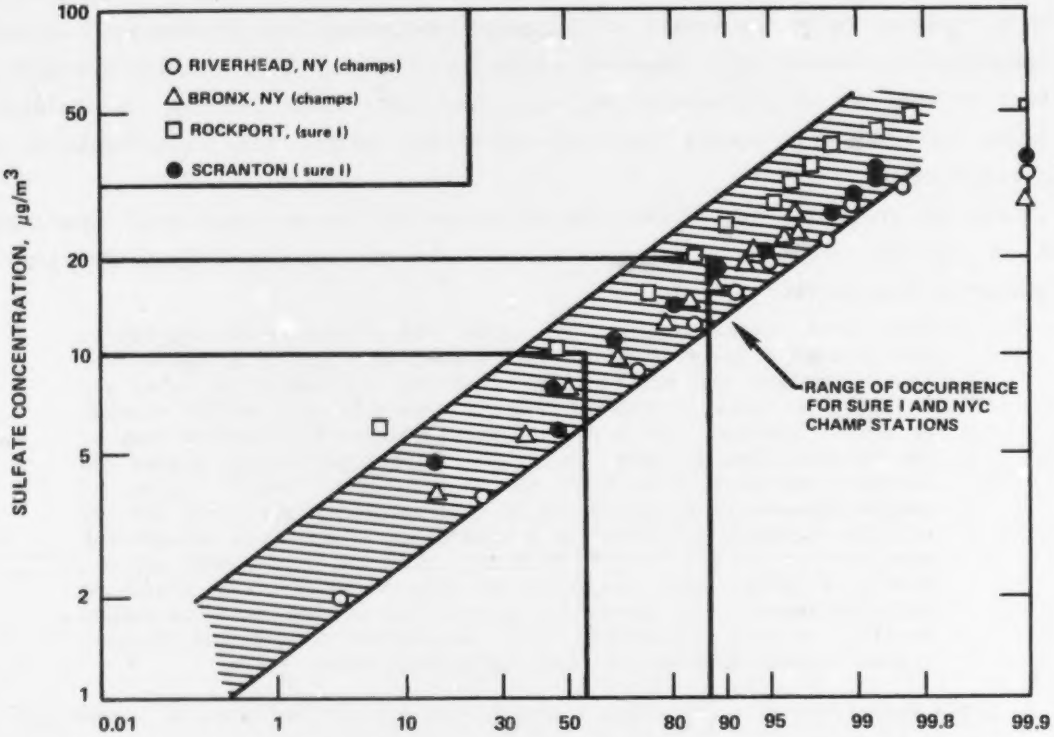


Figure 5-31. Cumulative plots show the frequency of sulfate concentrations in the SURE region on the basis of the 1974-75 historical data.

Source: Mueller et al. (1979).

Figure 5-32 shows the estimated number of days exceeding 10 μg/m^3 for August 1977 and January to February 1978. In August, almost the entire Northeast had at least 10 days with SO_4^{2-} concentrations greater than 10 μg/m^3. The area having 20 or more days with more than 10 μg/m^3 involved Ohio, West Virginia, Maryland, Pennsylvania, and New York. By contrast, in the winter months the area of prolonged elevated SO_4^{2-} concentrations shifted toward the West and Southeast. The upper Ohio Valley remained high, and an increase in the number of days with more than 10 μg/m^3 also occurred over Tennessee, Alabama, and Georgia.

Studies of seasonal variations have reported elevated concentrations in the summer months (Hitchcock, 1976; Hidy et al., 1978). The summer monthly mean concentrations of SO_4^{2-} in some regions can be twice those for the winter months. The seasonal variation in SO_4^{2-} concentrations in Southeastern and Midwestern cities is less distinct than the variation in New York City or Los Angeles (see Figures 5-33 and 5-34). Elevated summertime SO_4^{2-} concentrations are generally reported to be the result of increased homogeneous and heterogeneous oxidation of anthropogenically produced SO_2. However, oxidation of biologically produced hydrogen sulfide has been offered as an explanation for some high SO_4^{2-} concentrations in isolated areas (Hitchcock, 1976, 1977; Hitchcock, Spiller, and Wilson, 1980). (See also Chapter 2 relative to H_2S oxidation.)

Lavery et al. (1979) postulated the existence of two meteorological conditions that result in regional accumulation of particulate SO_4^{2-} concentrations above 20 μg/m^3 in the northeastern United States:

> The first regime consists of cases where widespread stagnation occurs with a large high pressure area slowly moving eastward over the midwestern and eastern United States. Zones of polluted air collect over areas within 100-300 kilometers of high sulfur dioxide emissions sources. These zones maintain themselves over periods of one to four days in warm, moist air, with light winds, around the southern and western parts of the high pressure area. The second regime appears to be conducive to long-range (greater than 500 km) sulfate transport and involves a channeling of air flow between the west side of the Appalachian Mountains and weak cold fronts approximately oriented west-southwest to east-northeast and traveling south-eastward. The channeling appears to be combined with capped vertical mixing associated with subsidence around the frontal system. These episodes can last up to four days.

5.5.1.2 Urban Variations--The preceding discussion of spatial and temporal variations of SO_4^{2-} was derived for the most part from widely spaced rural monitoring stations. It is of interest to note spatial variations on the much smaller scale of a metropolitan area. The SO_4^{2-} measured on this scale may consist of a natural background component, a long-distance transported component, a component formed locally in the atmosphere, and/or an artifact formed on the filter. Hidy et al. (1978) compared urban SO_4^{2-} distributions from the previously reported works of Lynn et al. (1975) for the New York City area, and Kurosaka (1976) did the same for the Los Angeles area. These areas differ in meteorology and climate, but the population and total SO_2 emissions are similar.

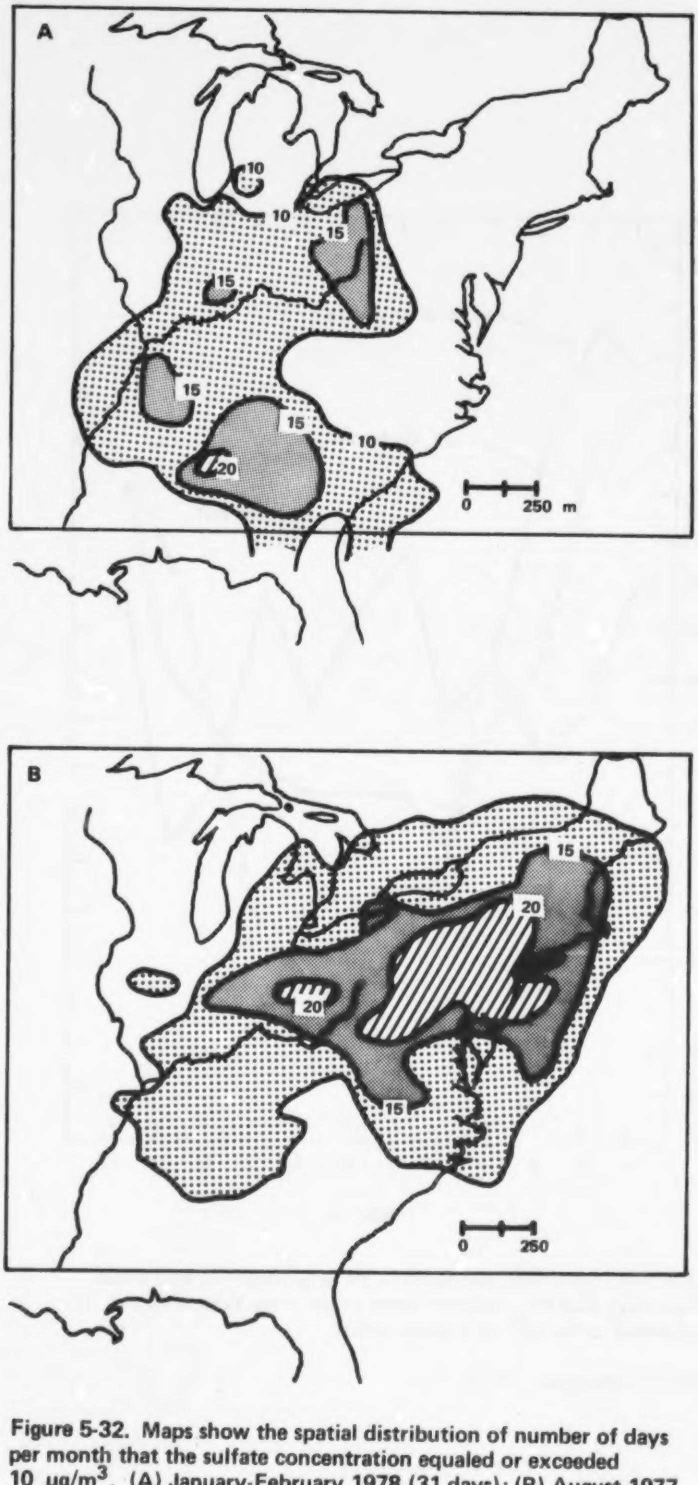

A
10
10
15
15
15
15
10
20
0
250 m
B
15
20
20
15
0
250

Figure 5-32. Maps show the spatial distribution of number of days per month that the sulfate concentration equaled or exceeded 10 $\mu g/m^3$. (A) January-February 1978 (31 days); (B) August 1977 (31 days).

Source: Mueller et al. (1979).

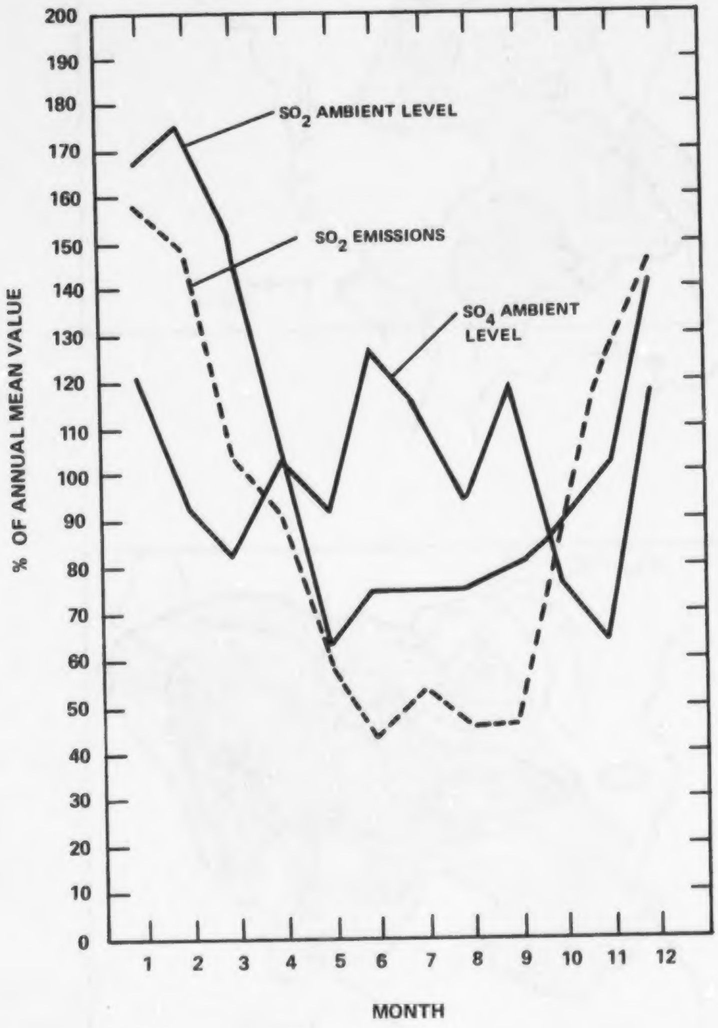


Figure 5-33. 1977 seasonal patterns of SO_2 emissions and 24-hr average SO_2 and SO_4 ambient levels in the New York area are normalized to the annual average values.

Source: Lynn et al. (1975).

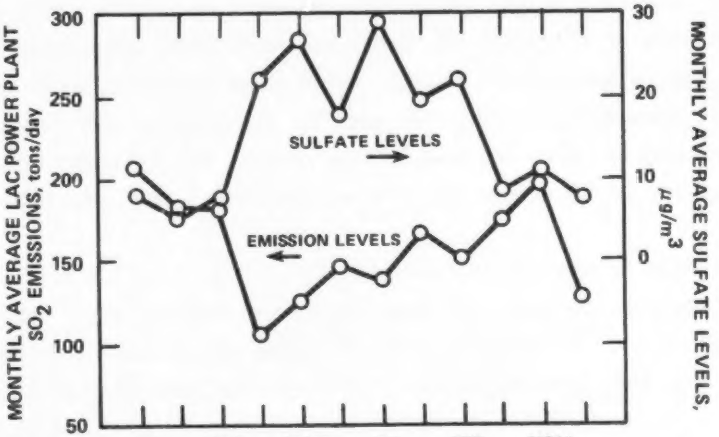


Figure 5-34. Monthly variation in monthly mean of 24-hr average sulfate concentration at downtown Los Angeles is compared with monthly mean 1973 Los Angeles County power plant SO_2 emissions.

Source: Hidy et al. (1978).

The population density of New York City is greater than that of Los Angeles (see Table 5-10). In addition, the emission patterns are dissimilar. As seen in Figure 5-35, there was a significant difference in SO_4^{2-} concentrations across the New York urban area, with the highest values observed in a strip from Staten Island northeast into Brooklyn. This finding may have been biased by the wintertime emissions; in summer, fairly uniform SO_4^{2-} concentrations have been found in the New York metropolitan area. The highest density of SO_2 emissions were in eastern New Jersey, Staten Island, Brooklyn, and Manhattan. Within a distance of 10 to 50 km from the sources of highest SO_2 concentration, the SO_4^{2-} concentrations decreased by 30 to 40 percent from their maximum values.

As shown in Figure 5-36, the mean annual average concentrations derived from 24-hour values in Los Angeles showed a relatively uniform distribution across the Los Angeles basin area. A weak maximum was found near Burbank and another in the San Bernardino area. The areas of major SO_2 emissions were El Segundo, Long Beach, and Fontana. One similarity to New York was found in the Los Angeles area; at distances exceeding 50 km from highest concentration areas, the SO_4^{2-} levels dropped off significantly.

Spengler and Dockery (1979) measured sulfates in particles less than 3.5 μm in diameter using a network of 10 to 12 sites in each of six cities for periods of up to 2 years. Analysis of variance showed no significant variation among sites within the cities of Topeka, KS; Portage, WI; Kingston, TN; and Watertown, MA. Some slight variations occurred among the sites in St. Louis, and significant variations occurred among the sites in Steubenville, OH. Only the Carondolet area of southeast St. Louis was monitored, not the entire city. There are a coke plant and a lead pigment plant nearby, which cause large SO_2 gradients and perhaps also SO_4^{2-} gradients. In Steubenville, the TSP and SO_2 values near the river were approximately twice the concentrations 5 km to the west of the river. For sulfates in this size range, the pattern was similar and the gradient was not as pronounced, but the differences among sites were significant.

An attempt was made to explain the variability in SO_4^{2-} data for both the Los Angeles area and the New York City area by means of stepwise linear regression. Table 5-11 displays the three principal independent variables and the r values associated with them in explaining the variance of the daily SO_4^{2-} concentrations. The results were very consistent in both areas except for Vista, CA, a community about 100 miles southeast of Los Angeles.

The results indicated that the most important variables were the 24-hour O_3 level, the midday RH, and the total particulate mass concentration, minus the SO_4^{2-} and nitrate fraction. Hidy et al. (1978) also suggested that these three factors were important in determining the daily variations of SO_4^{2-} concentrations. The O_3 or oxidant levels are an indication of photochemical oxidation, the RH is an indication of water content of the air mass, and TSP is an indication of reactions involving PM.

TABLE 5-10. SOME CHARACTERISTICS OF POLLUTION IN THE NEW YORK AND LOS ANGELES AREAS

Parameter	Los Angeles	New York
Surface area considered,[a] km^2	21,000	17,000
Population estimate (1970)	9,000,000	12,000,000
Population density, no./km^2	430	710
SO_2 emissions, tons/yr[b]	238,000	266,000
SO_2 emission density, kg/km^2/yr	10,300	14,200
Maximum temperature, °C[c]	22.8 (5.5)[d]	15.0 (7.4)
Minimum temperature, °C[c]	10.8 (4.6)	9.3 (8.4)
Relative humidity, %[e]	50.2 (17.0)	59.6 (16.5)
Normal precipitation, cm	36	106
Mean wind speed, m/sec[f]	3.3 (1.4)	5.8 (2.3)
Mixing height, m[g]	849 (472)	1290 (906)
Ventilation, m^2/sec	2690 (2160)	7460 (6200)
SO_2, μg/m^3 [h]	12.5 (19.9)	42.9 (45.0)
Water-soluble sulfate (SO_4^{2-}), μg/m^3 [h]	10.1 (7.9)	8.9 (5.7)
NO_2, μg/m^3 [h]	83.9 (44.3)	67.6 (36.0)
Water-soluble nitrate (NO_3^-), μg/m^3	9.1 (7.7)	2.6 (2.1)
O_3, μg/m^3 [h]	52 (34)	20 (22)
Total PM concentration (TSP) less SO_4^{2-} and nitrate, TSPM, μg/m^3	64.5 (27.4)	40.4 (19.9)

[a] Greater metropolitan areas; Los Angeles, South Coast Air Basin; New York, tri-state metropolitan area.
[b] Based on EPA Air Quality Control Regions.
[c] Annual mean of daily maximum or minimum hourly temperature.
[d] Numbers in parentheses are standard deviations.
[e] Annual mean of daily minimum humidity.
[f] Annual mean of noon wind speed at surface.
[g] Defined by annual mean of daily midday radiosonde sounding.
[h] Annual mean of 24-hr averaged values, 1974-75; Los Angeles, seven stations, New York, four stations.

Source: Hidy et al. (1978).

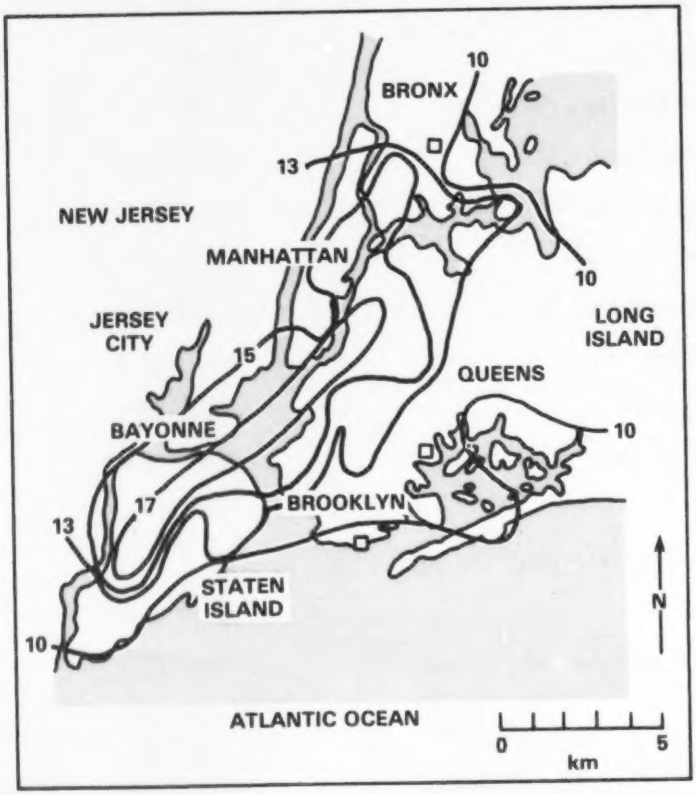

10
BRONX
13
NEW JERSEY
MANHATTAN
10
LONG ISLAND
JERSEY CITY
15
QUEENS
10
BAYONNE
17
BROOKLYN
13
STATEN ISLAND
N
10
ATLANTIC OCEAN
0
5
km

Figure 5-35. Map shows annual mean 24-hr average sulfate levels in micrograms per cubic meter in the New York area, based on 1972 data from Lynn et al. (1975). Squares are locations of three CHAMP site stations. The fourth station is at the tip of Long Island about 160 km from Manhattan.

Source: Hidy et al. (1978).

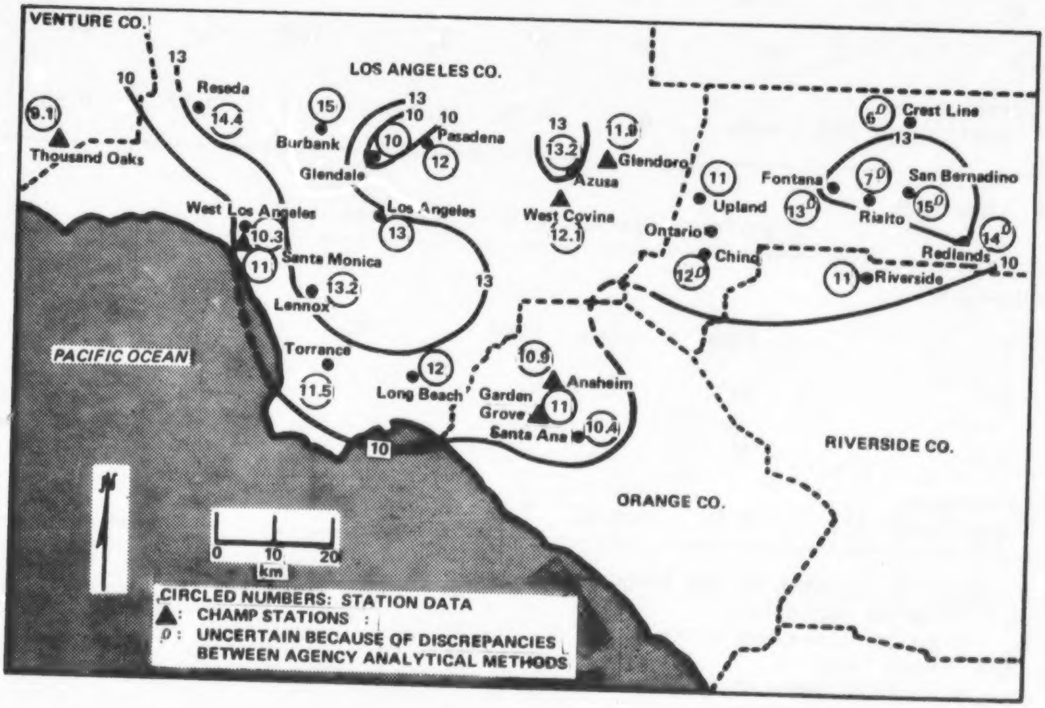

VENTURE CO.
LOS ANGELES CO.
ORANGE CO.
RIVERSIDE CO.
PACIFIC OCEAN
9.1
Thousand Oaks
10
13
Reseda
14.4
15
Burbank
13
10
10
Glendale
10
Pasadena
12
13
13.2
11.8
Glendora
Azusa
West Covina
12.1
11
Upland
Ontario
Chino
12ρ
Fontana
13ρ
6ρ
Crest Line
13
7ρ
Rialto
San Bernadino
15ρ
14ρ
Redlands
10
11
Riverside
West Los Angeles
10.3
11
Santa Monica
Los Angeles
13
13.2
Lennox
13
Torrance
11.5
12
Long Beach
10.9
Anaheim
Garden Grove
11
Santa Ana
10.4
10
N
0
10
20
km
CIRCLED NUMBERS: STATION DATA
▲: CHAMP STATIONS
ρ: UNCERTAIN BECAUSE OF DISCREPANCIES BETWEEN AGENCY ANALYTICAL METHODS

Figure 5-30. Distribution of annual average sulfate concentration in micrograms per cubic meter in the greater Los Angeles area is based on 1972-74 data.

Source: Kurosaka (1976).

TABLE 5-11. PRIMARY RANKING OF VARIABLES FOR CORRELATING AIRBORNE SO_4^2 IN TWO CITIES BASED ON A STEPWISE LINEAR REGRESSION OF 15 VARIABLES FROM CHAMP AND RELATED MONITORING STATIONS

A. Los Angeles area

	Anaheim	Garden Grove	West Covina	Glendora	Santa Monica	Thousand Oaks	Vista[a]
Variable							
1	O_3	O_3	O_3	TSPM	O_3	TSPM	T_{min}
2	TSPM	TSPM	TSPM	RH	RH	RH	O_x
3	RH	RH	RH	O_3	TSPM	O_3	RH
Correlation coefficient (R)	0.71	0.77	0.79	0.79	0.79	0.72	0.56

B. New York

	Brooklyn	Queens	Bronx	Riverhead, L.I.
Variable				
1	TSPM	TSPM	TSPM	TSPM
2	RH	RH	O_3	RH
3	O_3	O_3	RH	O_3
Correlation coefficent (R)	0.60	0.63	0.54	0.62

[a] Located 50 km north of San Diego and 16 km inland from the coast.

RH = Relative humidity.

O_3 = 1-hr daily maximum ozone value.

TSPM - Mean TSP.

T_{min} = Minimum temperature.

Source: Hidy et al. (1978).

The local SO_2 concentrations did not enter into the correlation sequence as one of the three principal variables. The findings of Spengler et al. (1979) are not inconsistent with these results, since the only city with a significant spatial variation among sites for sulfates also had a variation among sites for the respirable particles and TSP.

5.5.2 Nitrates

Nitrate aerosols make up a varying amount of the TSP. Although widely reported to be significantly less than the SO_4^{2-} fraction, nitrates nevertheless represent an important constituent. Most nitrates in the atmosphere are formed in gas-to-aerosol reactions, principally involving nitrogen dioxide and nitric oxide. These reactions may yield HNO_3 (gas or aerosols), ammonium nitrate, sodium nitrate, and lesser amounts of other compounds. A minor fraction of the NO_3^- aerosols measured in the atmosphere can be attributed to wind erosion of soil and resuspension of fertilizers (National Research Council, 1978b). These sources may be more important locally near fertilizer plants, transfer facilities, or munition factories (National Academy of Sciences, 1977).

Measurement of particulate NO_3^- has proved especially difficult (see Chapter 3). It has been clearly shown that gaseous HNO_3 is absorbed by glass-fiber filters (Pierson et al., 1980a; Spicer et al., 1978; Appel et al., 1979) and, consequently, NO_3^- values measured with such filters might be erroneously high when interpreted as reflecting particle composition. On the other hand, ammonium nitrate has significant vapor pressure and could be lost from some media by evaporation or by acid attack (Pierson et al., 1980a). There exists considerable controversy over the interpretation of available analytical data for NO_3^-, but the weight of current opinion appears to favor the idea that glass-fiber filter NO_3^- may be the sum of particulate nitrate and gaseous HNO_3. This issue is not yet settled, nor could any sort of consensus be said to exist. Still, the available data do indicate those regions with elevated levels of some NO_3^- species, either gaseous or particulate, previously measured as TSP mass.

Mean NO_3^- aerosol concentrations from urban and nonurban NASN sites are summarized in Figures 5-37 and 5-38, respectively. The annual average concentrations shown are in micrograms per cubic meter, as measured from hi-vol samples. Concentrations in urban air were substantially higher than those in nonurban air. A zone of high urban concentrations exceeding 4 $\mu g/m^3$ extended eastward from Chicago through the industrialized Northeast through Pennsylvania to the Philadelphia area. Other high NO_3^- zones were in southern Louisiana, around Birmingham, AL, and near Little Rock, AK. In general, a zone of high urban nitrate concentrations 3 $\mu g/m^3$ and higher extended from southeastern Texas through the Midwest and into the Northeast. Of course, a major emission source may cause high NO_3^- gradients in the surrounding area. For example, a study in Chattanooga, TN, (Helms et al., 1970; National Academy of Sciences, 1977) showed an average NO_3^- concentration of 48.9 $\mu g/m^3$ for a site close to the Volunteer Army Ammunition Plant. This is more than three times the NASN maximum station average for 1965 (13.5 $\mu g/m^3$). This station average was 15 to 20 times higher than those of the four other

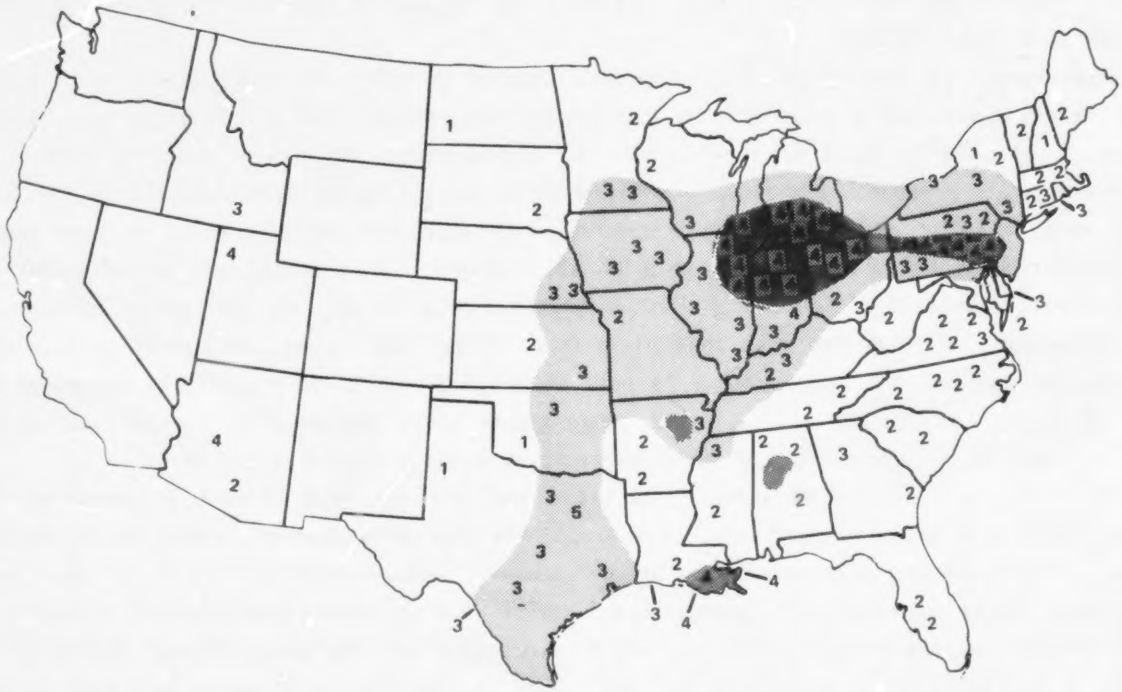


Figure 5-37. Map shows U.S. mean annual ambient nitrate levels in micrograms per cubic meter.

Source: Akland (1977).

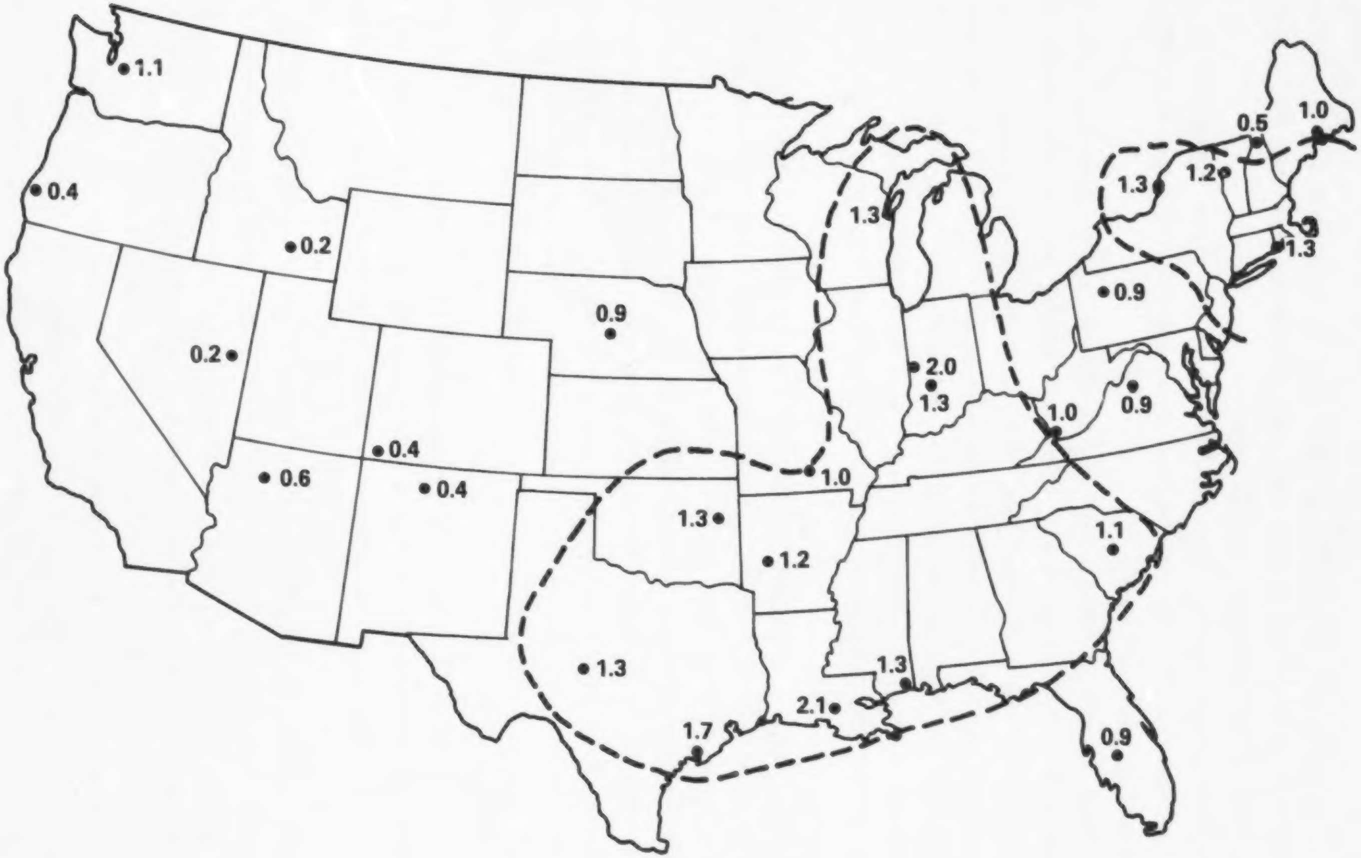

1.1
0.4
0.2
0.2
0.4
0.6
0.4
0.9
1.3
1.2
1.3
1.7
1.0
1.3
2.0
1.3
2.1
1.3
1.0
0.9
1.1
0.9
0.9
1.3
1.2
0.5
1.0
1.3

Figure 5-38. Mean nitrate concentrations in micrograms per cubic meter at nonurban sites in the U.S., based on valid annual averages from 1971 through 1974.

Source: U.S. Environmental Protection Agency (1977).

Chattanooga sites presumably not influenced directly by the munitions plant. Their averages ranged from 2.4 to 3.8 μg/m^3. While the artifact phenomenon may discredit the absolute values, the ratios among sites have more credibility.

It is obvious from these figures that the data base is quite incomplete for the West Coast. No data were reported for the Los Angeles area, nor for the large metropolitan areas of San Francisco, Seattle, and Portland.

A few studies have sought information on NO_3^- concentrations by composition and particle size. Orel and Seinfeld (1977) compared the formation, sizes, and concentrations of ambient SO_4^{2-} and NO_3^- particles. Unlike H_2SO_4, the HNO_3 that is formed tends to remain in the gaseous phase, although it may be an important component of acid precipitation. The EPRI SURE Project (Kneip et al., 1979) reported NO_3^- ion concentrations one-tenth the concentration of SO_4^{2-} ions. The monthly mean values for August and October 1977 were less than 0.6 μg/m^3 ammonium nitrate at three locations across the Northeast. On a few occasions the daily levels exceeded 1.5 μg/m^3.

Data from the SO_4^{2-} and NO_3^- data base of the California Aerosol Characterization Experiment are reported by Appel et al. (1978). Summer measurements for 1972 and 1973 from five fixed and one mobile site indicate that the mass median diameter for nitrates was between 0.3 and 1.6 μm. Twenty-four-hour averaged concentrations of NO_3^- ion varied across the Los Angeles basin, from a low of 4 μg/m^3 in Dominguez Hills to a high of 31 μg/m^3 in the eastern community of Rubidoux. In contrast to SO_4^{2-} the diurnal pattern for NO_3^- often had a maximum during the morning close to the maximum for gas-phase nitrogen oxides. The authors concluded that the ratios of ionic constituents and ambient NH_3 levels suggested that ammonium salts were the principal form of SO_4^{2-} and NO_3^-.

Until recently such high NO_3^- levels were not suspected in other parts of the United States. However, the EPA early analyses from a sampling program in Denver, CO, found 24-hour NO_3^- levels, primarily in the fine fraction, that often exceeded 10 μg/m^3 (Courtney et al., 1980).

Japanese workers have been investigating atmospheric nitrates for some time. Kadawaki (1977) found a bimodal distribution of nitrates in the Nagoya area of Japan. Submicrometer particles (0.4 to 0.6 μm in diameter) were ammonium nitrate; the coarse particles (3 to 5 μm in diameter) were sodium nitrate. Background nonurban levels as low as 0.8 to 0.9 μg/m^3 on the outer islands of Japan have been reported (Kito, 1977). Maximum average concentrations in the city of Kawasaki were reported to be as high as nearly 7 μg/m^3 (Terabe, 1977).

In summary, our knowledge of nitrates in the atmosphere is rather limited. No comprehensive data set exists. The NASN measures NO_3^- ion every 12 days at relatively few sites; spatial and short-term temporal variations cannot be discerned. In fact, there are many cities for which no measured values of nitrates have been reported. Furthermore, historic data before 1977 are in doubt because of the artifact formation on the filters.

There are spatial patterns in NO_3^- concentrations. Cities tend to have higher levels of nitrates than do rural regions. Some studies indicate that localized areas may have substantially higher NO_3^- levels. This raises the concern that available data on NO_3^- concentrations may underestimate the actual population exposure. In the near future, new sampling and analysis techniques should expand our knowledge of NO_3^- aerosols, HNO_3, and other nitrogen compounds.

5.5.3 Carbon and Organics

A variety of carbon-containing compounds often account for a large but highly variable portion of fine PM. Elemental carbon, which is emitted from a variety of combustion sources, is a significant component also, usually accounting for 10 to 20 percent of urban aerosol mass.

Organic substances of biological origin occur in particles. Evidence from microscopic examination of particles, cited later in this chapter, has demonstrated the presence of wood, paper, insect parts, pollen, bits of leaf, and textile fibers in coarse particle fractions. For the most part, these materials are made up of cellulose and protein, biologically derived substances that are insoluble in common organic solvents and that decompose to form carbon residues under thermal treatment. Analysis techniques capable of distinguishing this biologically fixed form of carbon from combustion-formed soot are only now becoming available (Huntzicker et al., 1982; Novakov, 1982; Wolff et al., 1982).

Organics in particles usually have been determined by extraction in organic solvents or by thermal evolution of organic vapors, procedures that concentrate relatively low molecular weight organic components. Consequently, there is little chemical analytical information relative to the organic high-polymer composition of particles, either those of biological or manmade origin. In the following discussion, the reader is cautioned that most studies have concentrated on these simpler organic molecules and do not entirely account for organic material in particles.

Particles emitted from combustion sources frequently have fuel-derived organic substances sorbed on their sources (see Chapter 4), and such materials are commonly found in the atmosphere. Combustion processes often alter fuel molecules considerably and combustion product mixtures often contain substances not in the fuel. Some examples include products of coal and wood pyrolysis, oxidized or nitrated hydrocarbons in motor vehicle exhausts, and synthesis of polynuclear aromatic hydrocarbons in rich flames. Chapter 4 covers many of these processes.

Photochemical reactions are also capable of generating substantial quantities of organic particles, and high concentrations of solvent-extractable PM are found associated with high O_3 levels. It is now believed that atmospheric oxidation of some volatile organic species leads to formation of bifunctional molecules, especially dicarboxylic acids, of very much lower vapor pressure than their precursors. These reactions are discussed in considerable detail in Chapters 2 and 6.

In addition to the organic species accounting for aerosol mass, there are also present in the particles very much smaller amounts of polynuclear aromatic hydrocarbons, components of special interest because several are known to be carcinogenic. One of these compounds, benzo(a)pyrene was conventionally measured in NASN TSP samples. A complete discussion of these substances is contained in the EPA Health Assessment Document for Polycyclic Organic Matter (Santodonato et al., 1979) to which the reader is referred.

Several comprehensive reviews of airborne-organic PM have appeared recently (National Academy of Sciences, 1972; Duce, 1978; Daisey, 1980; Hahn, 1980; Lamb et al., 1980). The subject has also been discussed in other reviews (National Academy of Sciences, 1976; Perera and Ahmed, 1978; Grosjean, 1977).

5.5.3.1 Physical Properties of Particulate Organics--Many atmospheric organic compounds are distributed between the vapor and particulate phases of the aerosol (De Wiest and Rondia, 1976; Krstulovic et al., 1977; Cautreels and Van Cauwenberghe, 1978), and, presumably, this distribution can vary with temperature. Because of this volatility, there can be substantial losses of low molecular weight compounds during sampling (Cautreels and Van Cauwenberghe, 1978; Krstulovic et al., 1977; De Wiest and Rondia, 1976; Katz and Chan, 1980; Schwartz et al., 1981). At the high temperatures found in combustion sources, larger proportions of the emitted organic compounds will be present in the vapor phase. These compounds will condense on the surface of PM as the emissions cool and, thus, be enriched at the surface. Natusch (1976) found that this occurs when PAH (polynuclear aromatic hydrocarbons) is emitted from powerplant stacks. Such surface enrichment can affect the biological impact of polycyclic organic matter (POM). While there is the possibility that POM may exist as particles formed by self-condensation, most POM is probably adsorbed on the surface of other particles, much of it presumably associated with soot particles (Thomas et al., 1968). The effect of the substrate upon which POM is adsorbed upon the chemical and biological reactivity of these compounds is almost entirely unknown. Korfmacher and coworkers (1980) recently reported that photodegradation of some PAH compounds proceeds much more slowly when the compounds are adsorbed on coal fly ash than when adsorbed on other substrates such as silica gel.

The distribution of organic particles between vapor and particulate phases is also profoundly influenced by chemical reactions in the atmosphere. Grosjean and Friedlander (1975) found that during photochemical oxidant incidents organic substances are converted from volatile to relatively nonvolatile species. In this process, the fraction of organic mass in the particle phase (relative to the gas) can grow from very low values, 1 percent or so, to about 6 percent of the vapor and particle total.

While both mass and size distribution of organic substances in particles is clouded by their volatility, there have been some attempts to establish the fine/coarse ratios. Some of the heavier polycyclic components are known to be predominantly fine-particle components (Mueller et al., 1964; De Maio and Corn, 1966; Kertèsz-Saringer et al., 1971; Pierce and Katz, 1975; De Wiest, 1978; Van Vaeck and Van Cauwenberghe, 1978, 1980). In Los Angeles oxidant incidents, virtually all the organic particles were found to be smaller than 2.5 μm (Schuetzle et al., 1975; Mueller et al., Hidy et al., 1975). Van Vaeck and Van Cauwenberghe (1978) reported that aliphatic hydrocarbons and carboxylic acids were predominantly (90 percent) in fine particles in European samples. Since organic compounds are generally distributed disproportionately in the fine fraction aerosols, it is not surprising that they represent an important fraction of the mass. Steigerwald (1975) estimated that organic substances are between 25 and 47 percent of the fine particle fraction in the United States. However, there are also reports of significant fractions of organic substances in coarse particles in rural samples (Stevens et al., 1982). No consistent study of organic species or classes by particle size exists in the literature. Therefore, it is currently impossible to trace the origins and fate of organic particle components or area or timewise distributions on the basis of ambient air measurements.

5.5.3.2 Carbon and Total Organic Mass--There are limited historical data on the mass fraction of elemental carbon in atmospheric aerosols, but very recent work is contributing information in this area (Rosen et al., 1982; Novakov, 1982; Wolff et al., 1982; Huntzicker et al., 1982; Stevens et al., 1982; Lewis and Macias, 1980; Stevens et al., 1980). Techniques currently employed detect both organics and carbon by optical absorption and selective combustion techniques.

Novakov (1982) found elemental and organic carbon in over 1000 samples collected from a variety of urban sites. In New York City, the principal chemical species present was elemental carbon, accounting for two-thirds or more of the carbon mass; the balance was organic. In Denver, about 60 percent was elemental carbon, while in Los Angeles about 70 percent was organic and the balance, elemental carbon.

Wolff et al. (1982), using a somewhat different technique, reported carbon concentrations in 10 U.S. locations. "Apparent" elemental carbon was reported to range from 1.1 $\mu g/m^3$ in a remote South Dakota location to 13.3 $\mu g/m^3$ in New York City. These values covered a range of 4 to 11 percent of the TSP.

Stevens et al. (1980, 1982) and Lewis and Macias (1980) reported total carbon values of 8.4 $\mu g/m^3$ (14 percent of total dichotomous sample mass) in Charleston, WV, while in the Great Smoky Mountains and Shenandoah Valley only 1.2 $\mu g/m^3$ and 1.5 $\mu g/m^3$, respectively (4 percent of total dichotomous sample mass in both cases), was elemental carbon and 3.4 $\mu g/m^3$ and 0.9 $\mu g/m^3$, respectively (12 percent and 3 percent of total dichotomous sample mass), was organic carbon.

The mass of organic substances present in atmospheric aerosols was at one time approximated by solvent-extraction with benzene in routine NASN hi-vol samples. Other solvents have also been used in such determinations. Unfortunately, such determinations were terminated in 1970 and, except for a few intensive studies (Daisey, 1980; Grosjean and Friedlander, 1975; Wesolowski et al., 1980), there has been no extensive data base on organic extractables covering the past 10 years.

Some typical values for particle number and mass concentrations of organic substances are listed in Table 5-12. The organic fraction of the mass concentration as measured by the benzene-soluble component* is also listed, with the benzo(a)pyrene fraction for comparison. In the organic fraction, a variety of organic compounds have been identified, including some materials classified as PAH (Corn, 1968). However, the identified fraction represents only 10% of the organic components of the urban aerosol. Although the total aerosol number concentration is often very large in cities, the mass concentration varies less and rarely exceeds about 200 μg/m^3 in the United States. The benzene-soluble fraction of this is about 10-20 percent of the total mass, and the concentration of benzo(a)pyrene is far lower. Even in remote areas, there is a contribution of organic material.

A limited number of samples have been collected in unpolluted atmospheres. Levels in remote areas and in marine air for the ether-soluble fraction of organic particulate matter have been as low as 0.51 (0.18-0.84) μg/m^3 STP. Marine air with a continental influence had averages of 0.93 (0.48-1.38) μg/m^3 and continental air 1.2 (0.69-1.71) μg/m^3. Similar concentrations have been observed at Barrow, AK, a remote site in the Arctic, for cyclohexane- and dichloromethane-soluble POM (Daisey et al., 1981).

Variations in the concentration of organic particulate matter by location, meteorological conditions, season and by time of day have been observed repeatedly (Hidy et al., 1975; Gordon, 1976; Calvert, 1976). By way of illustration, Figure 5-39 shows the differing contributions of the organic fraction in samples obtained in two cities in southern California (National Academy of Sciences, 1972). In both instances, however, the organic fraction represents a sizeable portion of total suspended particulate material.

A pattern of elevated wintertime concentrations of organic particulate matter has been observed in New York City and in Mainz, West Germany. Winter samples in Mainz of ether-extractable organic material averaged 27 μg/m^3 for TSP concentrations averaging 150 μg/m^3. Winter samples collected in February, 1977 in New York City had a total extractable organic fraction of 22 μg/m^3 for a TSP average of 96 μg/m^3. The August, 1976 levels were 13.3 μg/m^3 for a TSP average of 86 μg/m^3 (Kneip et al., 1979).

A 1971 study of Colucci and Begeman is an example of a more detailed short-term urban survey of PAH than is available from NASN data. From 1964 to 1965, Colucci and Begeman (1971) found that the concentrations of benzo(a)pyrene and benz(a)anthracene were 4 1/2 times greater in central Los Angeles than at two suburban sites. However, the suburban site downwind of the downtown area (on the average) appeared to have systematically higher benzo(a)pyrene concentrations than the upwind site. Daily concentrations reported in the Los Angeles area ranged from 0.1 ng/m^3 to over 10 ng/m^3, depending on the season. Benz(a)anthracene concentrations were 1 1/2 times larger than the benzo(a)pyrene concentrations. Annual average benzo(a)pyrene concentrations were similar to the NASN data for downtown Los Angeles. The PAH

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*The benzene-soluble extract is not necessarily equivalent to the total amount of organic material in the sample, but it is taken to be representative of such a fraction.

TABLE 5-12. TYPICAL VALUES OF AEROSOL CONCENTRATION FOR DIFFERENT GEOGRAPHIC AREAS (ANNUAL AVERAGES)[a]

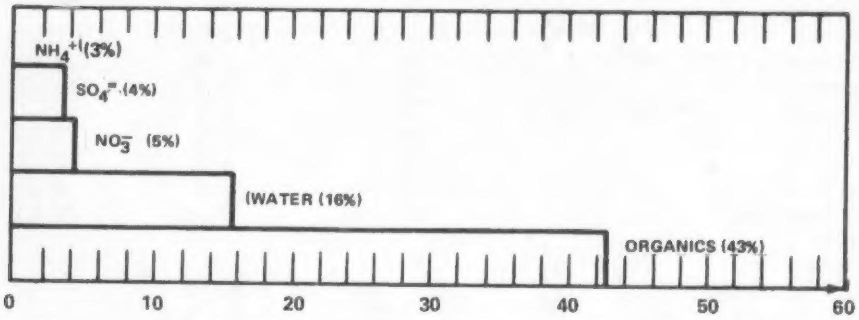
Location	Number of particles/cm^3[b]	Mass concentration, $\mu g/m^3$[c]	Benzene soluble fraction, $\mu g/m^3$	BaP fraction, ng/m^3
Nonurban				
Continental				
General	$10^3 - 10^4$	20 - 80	1.1 - 2.2	-
California	$10^3 - 10^4$	39	2.8	0.48
Oregon	-	47	0.9	0.09
Colorado	$10^3 - 10^4$	14	1.1	0.11
Indiana	-	39	2.1	0.25
Maine	-	18	1.2	0.12
New York	-	29	1.8	0.25
So. Carolina	-	40	2.7	0.43
Maritime				
General	$10^3 - 10^4$	-	-	-
Pacific offshore	$10^3 - 10^4$	19 - 146[d]	1.5 - 6.1[d]	-
Oahu, Hawaii	$10^3 - 10^4$	10 - 49[d]	0.7 - 6.3[d]	-
Urban				
Continental				
General	$10^3 - 10^4$	>100	7	-
Los Angeles	$10^3 - 10^4$	93	12.5	1.87
Portland	-	72	6.6	2.60
Denver	$10^3 - 10^3$	110	9.0	2.52
Minneapolis	$10^3 - 10^3$	70	6.1	1.18
Chattanooga	-	105	6.9	4.18
New York	-	105	3.9	3.63
Greenville, SC	-	76	7.4	7.49
Maritime				
Honolulu, Hawaii	$10^3 - 10^4$	40	2.3	0.59
San Juan, Puerto Rico	-	77	6.9	1.42

[a] Data based on 1969 NASN observations, except for maritime data.

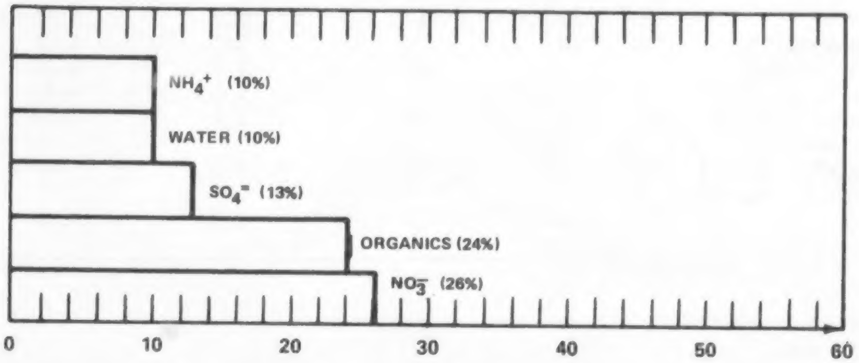
[b] Aitken nuclei

[c] Geometric means.

[d] Short-term data.



PASADENA, 9/20/72; TWO HOUR SAMPLE OVER 1200-1400 PST; LOW OXIDANT, TOTAL MASS CONCENTRATION, 79 $\mu g/m^3$.



POMONA, 10/24/72; SAMPLES FROM 1200-1400 PST; MODERATE OXIDANT, TOTAL MASS CONCENTRATION, 178 $\mu g/m^3$.

Figure 5-39. Calculated distribution of aerosol constituents for two aerosol samples taken in the Los Angeles basin.

Source: National Academy of Sciences (1972).

concentrations increased substantially in winter. Benzo(a)pyrene concentrations were higher at night, in contrast with those of other pollutants. All pollutants were higher on weekdays than on weekends. Benzo(a)pyrene concentrations were found to be correlated with carbon monoxide and lead concentrations, with coefficients ranging from 0.6 to 0.9. Benzo(a)pyrene concentrations were also significantly related to those of hydrocarbon vapors, oxides of nitrogen, and vanadium (a nonautomotive pollutant). Despite the strong relation to lead, the statistics in the study failed to reveal a clear identification of BaP emissions with automotive or stationary combustion sources.

Trends of BaP concentrations as measured at 34 NASN urban sites are displayed in Figure 5-40. It is indeed encouraging to see the steady decline in BaP concentrations that has occurred since the mid-1960's. The 90th percentile of quarterly measurements fell dramatically from near 7 ng/m^3 to less than 2 ng/m^3. These changes reflect both emission controls and shifting of sources. Incomplete combustion of fossil fuels, especially coal, is a primary source of BaP. Major point and area sources include residential coal-fired furnaces, coal-fired utilities and industrial boilers, coke ovens, petroleum refineries, and incinerators (see Chapter 4). Shifts away from coal for residential, commercial, and light industrial use have made a substantial contribution to the reduction of urban BaP concentrations. To a lesser extent, the control of particulate emissions has also helped to lower concentrations.

The national trends in benzene-soluble particulate matter and BaP as reported by Faoro (1975) may not be true everywhere. Indeed, specific organic fractions may show opposite trends. Daisey (1980) discussed benzene soluble organic trends for New York City; annual averages for the New York University station, normalized to account for year-to-year meteorological variations, are reported in Table 5-13.

TABLE 5-13. ANNUAL AVERAGES OF ORGANIC FRACTIONS IN TSP
NEW YORK CITY[a], DISPERSION NORMALIZED

Year	TSP, μg/m^3	Organic fraction[b] μg/m^3	Percent organics in TSP
1968	95.7	10.2	10.6
1969	129	10.8	8.4
1977-78	59.8	8.8[c]	14.7

[a] NYU Medical Center Station.

[b] Total of nonpolar (benzene-soluble) and polar (acetone-soluble) organics.

[c] Respirable (≤3.5 μ) organics only.

Source: Daisey (1980).

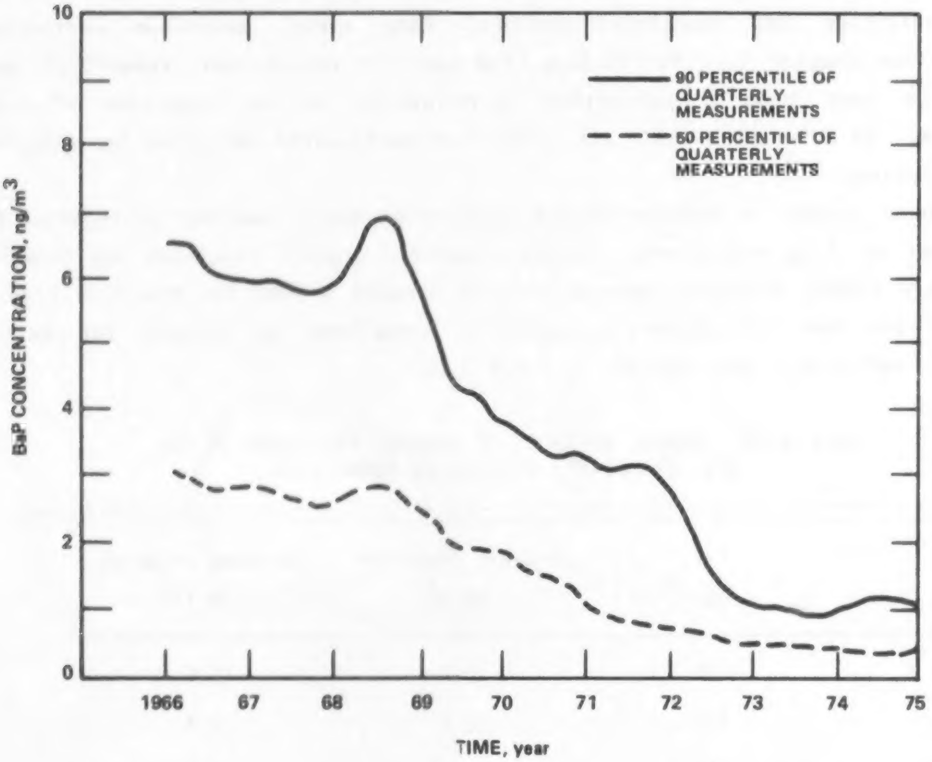


Figure 5-40. Benzo(a)pyrene seasonality and trends (1966 to 1975) in the 50th and 90th percentiles for 34 NASN urban sites.

Source: U.S. Environmental Protection Agency, 1979.

Although TSP had decreased by 40% between 1968 and 1978, the POM fraction decreased by only 10%.

5.5.3.3 Chemical Composition of Particulate Organic Matter--Particulate organic matter has often been fractionated by means of acid-base extractions followed by column chromatography (Hueper et al., 1962; Tabor et al., 1958; Hoffmann and Wynder, 1977; Asahina et al., 1972). The composition data for Detroit PM found in Table 5-14 are fairly typical and present the general proportions of various broad classes of compounds present. Hoffmann and Wynder (1977) found that the fraction containing PAH was principally responsible for the tumorigenic properties of POM in mice.

TABLE 5-14. COMPOSITION OF THE ORGANIC FRACTION OF AIRBORNE PM COLLECTED IN DETROIT[a]

Fraction	Percent of total extractable organic matter
Aliphatic hydrocarbons	48.3
Aromatic hydrocarbons[b]	3.6
Neutral oxidized hydrocarbons	20.8
Acidic compounds	14.8
Basic compounds	0.55
Insolubles	10.8

[a] 3 μg/m^3 annual average benzene-soluble organics.

[b] Including PAH.

TSP not reported.

Source: Hoffman and Wynder (1977).

Specific classes of compounds identified in the organic fraction of airborne PM include PAH,aromatic and aliphatic hydrocarbons, aza-arenes, aliphatic and aromatic aldehydes and ketones, quinones, phenols, polyols, phthalic acid esters, sulfur heterocyclics, aryl and alkyl halides, chlorophenols, nitro compounds, and alkylating agents (Hoffmann and Wynder, 1977; Daisey, 1980; Lamb et al., 1980). Of all the airborne organic compounds, the most information exists for the classes of POM. The greatest attention has been focused on the subclasses of PAH and the polycyclic heterocyclic compounds such as the aza-arenes, because many of the compounds in this class are potent carcinogens in animals. Some of the polycyclic hydrocarbons identified are pyrene, BaP, benzo(e)pyrene, benz(a)anthracene, perylene, chrylene, chrysene, coronene, fluoranthene, benzo(ghi)perylene, and alkyl derivates of these compounds (Sawicki et al., 1962; Sawicki et al., 1965).

Benzo(a)pyrene was one of the earliest compounds in this mixture of organic matter to be identified and routinely measured. Some measurements for BaP in the United States date to the early 1950's. Sawicki and coworkers in the 1960's extracted and identified many organic compounds. Today there is a renewed effort, using more sophisticated techniques and attempting to answer the many questions still remaining on the biological significance, variations and concentrations, specific source contributions, and the reactivity of airborne organic matter.

In 1972, the National Academy of Science published an extensive report on the biologic effects of airborne matter entitled Particulate Polycyclic Organic Matter (National Academy of Sciences, 1972). According to the report, emission source data for airborne organic substances are generally expressed in terms of estimated BaP emissions. Benzo(a)pyrene is used as a surrogate for detecting the presence of airborne organic pollutants because it appears to be a prominent constituent of POM. Benzo(a)pyrene is also a known animal carcinogen and the best documented of all the polycyclic organic compounds (National Academy of Sciences, 1972). It cannot be regarded as a perfect indicator of polycyclic aromatic hydrocarbons in the air nor of their carcinogenic properties; however, because better data are generally not available, BaP is presently used as an indicator of the potential carcinogenicity of general air pollution (Bridbord, et al., 1976).

Despite much work on certain subfractions of POM, such as the polycyclic organic fraction, other compound classes such as the oxidized hydrocarbons remain relatively unexplored. Sawicki (1976) has estimated that "over 99% (sic) of the organic pollutants in the air have never been determined."

In photochemical incidents, volatile hydrocarbons are converted to very large quantities of 5 to 7 carbon bifunctional carboxylic acids (Schuetzle et al., 1975; Grosjean and Friedlander, 1975; Cronn et al., 1977). Schuetzle et al. (1975), in a report of a 1972 incident, state that alkanes and alkyl naphthalenes accounted for 1.5 to 3 percent of the fine particle mass, and bifunctional compounds amounted to about 11 percent. In addition to glutaric, adipic, and pimelic acids, the corresponding hydroxy carboxylic acids and a variety of their nitrate and nitrite ester derivatives were reported.

Cronn et al. (1977) confirmed those findings in a series of sub-3.5 μm samples taken during the 1973 California Air Characterization Experiment. These authors found levels of organic particulate matter up to 65 $\mu g/m^3$ out of a fine-particle loading of 230 $\mu g/m^3$. These substances included small amounts of alkanes, alkyl naphthalenes, and piperidines (up to 12 $\mu g/m^3$) and much larger quantities of C_5 to C_7 dicarboxylic acids, hydroxy-acids, and amides.

Grosjean and Friedlander (1975) have found organic extractables of 141 $\mu g/m^3$ during an incident in 1973; one-half to one-third of this mass was polar organics. These organic substances together with ammonium sulfate and nitrate accounted for 95 percent of the secondary aerosol during photochemical incidents. Therefore, there is substantial evidence that organic particles can be influenced in a very major way by photochemistry.

Classes of biologically active compounds other than PAH and related polycyclic organics have been identified in airborne PM. This includes alkylating agents, N-nitrosamines (Kneip et al., 1979), nitro derivatives of PAH (Jäger, 1978), and the compounds responsible for the mutagenic activity of POM in the Ames assay (Kneip et al., 1979; Talcott and Wei, 1977; Pitts et al., 1977; Daisey et al., 1979). In addition, there may also be unstable compounds present in the aerosol, such as epoxides and lactones (Van Duuren, 1972), that are significant for human health but decompose when collected by conventional sampling techniques. There is a need to identify specific compounds such as these, to evaluate their significance for human health, and to determine their sources and concentrations in the ambient atmosphere. There is also a need to identify sampling artifacts and develop improved sampling techniques for organic compounds in the aerosol.

5.5.4 Metallic Components of Fine Particles

It is useful to study not only the chemical but also the elemental composition of airborne particles. Many trace elements are known to be toxic and can act as catalysts in atmospheric reactions. Table 5-15 indicates the mean and maximum concentrations of several elements found in urban and nonurban areas in the United States from 1970 to 1974. Certain trace elements tend to be enriched in urban airborne particles relative to their concentration in fuels. For example, Table 5-16 lists the ratios of urban to suburban concentrations of trace elements in three groups. Since the ratio of urban to suburban TSP was 2.8, those elements with higher ratios (antimony through bismuth) were concluded to be mainly of urban origin. The middle group (mercury through calcium) had ratios near that of TSP and therefore occur equally abundantly in city and suburban particles. The remaining group (silicon through bromine) appeared mainly in suburban suspended particulate matter. As Table 5-17 indicates, they were not homogeneously distributed among the various particle size fractions. There was also spatial variability in the composition of the aerosol, as indicated by Table 5-18. These intercity differences reflect the difference in industries and types of fuel used in these urban areas.

Hi-vol filter samples from the NASN have been routinely analyzed for certain metals since the early 1960's. The data for certain metals for the years from 1965 to 1974 have been summarized in an EPA report (Faoro and McMullen, 1977). This report presents the composite national and regional trends for nine trace metals, fuel-related metals (lead, vanadium, nickel, and titanium) and industry-related metals (cadmium, chromium, copper, iron, and manganese). These trends were derived from samples collected from 92 urban and 16 nonurban NASN hi-vol stations.

The instrumental techniques for detecting metals changed in 1970, significantly improving the lower limits of detection. This report, in addition to Akland (1976) describes the

TABLE 5-15. COMPARISON OF URBAN AND NONURBAN ANNUAL AVERAGE CONCENTRATIONS FOR SELECTED METALS, 1970-74 ($\mu g/m^3$)

	Be[a]		Cd		Cr		Co		Fe		Pb		Mn		Ni		Ti		V	
	U[b]	NU[b]	U	NU	U	NU	U	NU	U	NU	U	NU	U	NU	U	NU	U	NU	U	NU
1970																				
Maximum	2.9	.24	.099	.0001	.130	.075	.014	LD	14.2	1.62	5.83	1.471	2.10	.068	.277	.097	.26	.093	1.222	.112
Arithmetic mean	LD[c]	LD	.003	.0001	.008	.003	LD	LD	1.7	.38	1.19	.088	.07	.015	.015	.005	.05	.013	.052	.008
Std. deviation	0.2	.03	.007	--	.011	.009	.001	--	1.3	.27	.80	.190	.12	.013	.028	.014	.03	.011	.116	.019
1971																				
Maximum	0.7	.24	.295	.0001	.171	.061	.085	LD	16.0	2.80	6.31	1.134	1.95	.102	.347	.083	.51	.069	1.325	.209
Arithmetic mean	0.1	.01	.004	.0001	.009	.004	.001	LD	2.1	.51	1.23	.047	.08	.018	.015	.003	.04	.017	.041	.007
Std. deviation	0.1	.03	.016	--	.014	.007	.003	--	1.6	.38	.87	.155	.11	.015	.028	.011	.05	.020	.108	.024
1972																				
Maximum	LD	LD	.112	.0001	.143	.039	.042	LD	6.4	1.15	6.88	1.048	.86	.046	.268	.082	.48	.092	.858	.205
Arithmetic mean	--	LD	.002	.0001	.006	.002	LD	LD	1.2	.25	1.13	.139	.04	.007	.011	.004	.04	.027	.022	.004
Std. deviation	--	--	.007	--	.010	.004	.002	--	.8	.22	.78	.169	.06	.009	.023	.012	.03	.022	.056	.019
1973																				
Maximum	LD	LD	.032	.0001	.228	.066	.027	LD	6.9	1.19	5.83	.939	.56	.030	.439	.280	.23	.084	.393	.035
Arithmetic mean	LD	LD	.001	.0001	.007	.003	.001	LD	1.1	.19	.92	.110	.04	.004	.014	.011	.04	.028	.016	.002
Std. deviation	LD	--	.003	--	.015	.009	.002	--	.8	.18	.64	.149	.05	.005	.037	.037	.03	.021	.034	.005
1974																				
Maximum	0.2	LD	.077	.0002	.073	.009	.029	LD	6.2	.69	4.09	.534	.35	.033	.639	.026	.22	.066	.248	.023
Arithmetic mean	LD	LD	.002	.0002	.006	.002	LD	LD	1.1	.24	.89	.111	.04	.006	.009	.002	.04	.020	.019	.002
Std. deviation	=	--	.005	--	.006	.002	.001	--	.7	.17	.57	.111	.04	.007	.029	.004	.03	.017	.037	.004

[a] expressed in ng/m^3; [b] U = urban; NU = nonurban; [c] LD = less than detectable. Source: G. Akland (1976).

TABLE 5-16. RATIOS OF URBAN (U) TO SUBURBAN (S) CONCENTRATIONS IN AIR, CLEVELAND, OH, AREA

Enriched in cities		Ratio similar to TSP		Enriched in suburban particles	
Element	U/S	Element	U/S	Element	U/S
Antimony	6.9	Mercury	3.0	Silicon, tin	1.8
Chloride	6.5	Iron	2.8	Copper, vanadium	1.8
Beryllium	6.1	Cadmium	2.5	Aluminum	1.7
Chromium	5.6	Sodium	2.4	Zinc	1.6
Cobalt	3.4	Magnesium	2.4	Arsenic	1.4
Bismuth	3.3	Manganese	2.2	Selenium	1.3
		Calcium	2.0	Bromine	1.2

Note: Mean TSP ratio = 2.8

Source: Economic Commission for Europe's Working Party on Air Pollution Problems (1977).

TABLE 5-17. CORRELATIONS OF CHEMICAL CONTENT WITH PARTICLE SIZE

a) Predominant particle size for various substances

Normally fine	Normally coarse	Normally bimodal	Variable
Sulfates	Iron, calcium	Chloride	Nickel
Organic (condensed vapors)	Titanium	Nitrate	Tin
Lead	Magnesium		Vanadium
Arsenic	Potassium		Antimony
Selenium	Phosphate		Manganese
Hydrogen ion	Silicon		Zinc
Ammonium salts	Aluminum		Copper
Soot	--		--

b) Ratios of element distribution between fine and coarse particles

(St. Louis urban aerosol, 18-day average, Aug. to Sept. 1975)

Predominantly fine		Predominantly coarse	
Element	Fine/coarse	Element	Fine/coarse
Sulfur	8.90	Calcium	0.09
Lead	3.67	Silicon	0.13
		Iron	0.29
		Potassium	0.33
		Titanium	0.55

Source: (a) Miller et al. (1979).
(b) Dzubay et al. (1977).

TABLE 5-18. PARTICULATE ANALYSES FROM SELECTED URBAN LOCATIONS

	Atlanta, GA	Birmingham, AL	Baltimore, MD	Albuquerque, NM
Suspended particles	97.	142.	146.	120.
Antimony	0.000	0.000	0.000	0.000
Beryllium	0.000	0.000	0.000	0.000
Bismuth	0.000	0.000	0.000	0.000
Cadmium	0.017	0.008	0.003	0.000
Chromium	0.002	0.005	0.018	0.001
Cobalt	0.000	0.000	0.000	0.000
Copper	0.04	0.06	0.06	0.07
Iron	1.2	1.7	0.8	a
Manganese	0.06	0.15	0.08	0.03
Nickel	0.007	0.004	0.034	0.000
Tin	0.02	0.01	0.01	0.01
Titanium	0.03	0.03	0.01	0.01
Vanadium	0.001	0.003	0.071	0.001
Zinc	0.52	1.09	0.34	0.00

[a] Not analyzed.

Arithmetic mean values for 1966 expressed as micrograms per cubic meter.

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Source: Corn (1976).

methods used and the implications for trends analysis. In general, the data presented indicate changes in atmospheric concentrations of various metals occurring in different regions of the country. For the most part, the reported trends are consistent with changes in emission patterns (due to industrial source control) and in fuel use.

Similar to trends in urban TSP concentrations, metals concentrations declined in most urban areas, with the exceptions of copper, titanium, and possibly chromium. Table 5-19 summarizes metal trends and possible causes for these trends. Both beryllium and cobalt had such very low concentrations that trends could not be identified with any certainty. Trends in other metals, such as vanadium and nickel, parallelled air pollution control regulations mandating the use of low-sulfur fuels. There was a drop in vanadium and nickel, particularly in the Northeast, because the desulfurization process of petroleum also removes these impurities. Titanium, on the other hand, may have increased because of the rise in coal use by utilities. Decreases in iron, manganese, and cadmium concentrations were probably the result of reduced particulate emissions from steel plants and related industries. Improved incineration methods and use of sanitary landfills instead of incinerators may also have contributed to the decrease. No trends were apparent for copper, but it is felt that the high concentrations were caused by contamination from the commutators of the high-volume samplers.

5.5.4.1 Lead--The seasonal patterns and trends in the quarterly averaged urban lead concentrations are displayed in Figure 5-41. The national composite 50th percentile of lead concentrations fell from about 1.1 $\mu g/m^3$ in 1971 to 0.84 $\mu g/m^3$ in 1974, approximately a 24-percent decline. This is attributed to decreased lead in gasoline and the drop in premium gasoline sales since 1970. Premium gasoline has, on the average, a higher lead content than regular gasoline. Lead concentrations are expected to continue to decrease in the future because of increased use of unleaded gasoline in new cars equipped with catalytic converters. This national decrease is not equally evident throughout the country, however, because of differences in growth rates and vehicle miles travelled. These results should be used with caution because of the small number of stations used in determining the trends. An NASN location in downtown Los Angeles experienced the highest lead concentrations, averaging between 4 and 5 $\mu g/m^3$ until 1971; the concentrations decreased to about 2 $\mu g/m^3$ in 1974. Again, while the reduction of lead content in gasoline and the increased use of lead-free gasoline may have contributed to this decline, the decrease in vehicle miles travelled in downtown urban areas also contributed to the decline. There is some evidence that rural sites have shown either stable or slightly increasing patterns in ambient air lead content in the United States.

5.5.4.2 Vanadium, Nickel, and Other Metals--Figure 5-42 shows, for the five broad geographical areas of the United States, the 90th percentiles of the annually averaged vanadium concentration. The Northeast had substantially higher vanadium concentrations than any other area of the United States. Over this 10-year period the concentrations of vanadium decreased

TABLE 5-19. TRENDS IN REPORTED URBAN METAL CONCENTRATIONS AND THEIR POSSIBLE CAUSES

Metal	Observed trends	Possible causes
Fuel combustion-related metals:		
Beryllium	Unknown	--
Lead	Down; expected to decrease further	Lower lead content in gasolines after 1969
Nickel	Down	Reduction of Ni in residual oils
Titanium	Up	Increasing use of coal in electric utilities
Vanadium	Down	Reduction of V in residual oils
Industry-related metals:		
Cadmium	Down	Controls in metal industry and improved incineration practices
Chromium	No trend	Unknown
Cobalt	Unknown	--
Copper	No trend	Contamination from hi-vol commutator
Iron	Down	Improved incineration or waste burning practices, fuel switching, controls in steel industry
Manganese	Down	Controls in metals industry

Source: Faoro and McMullen (1977).

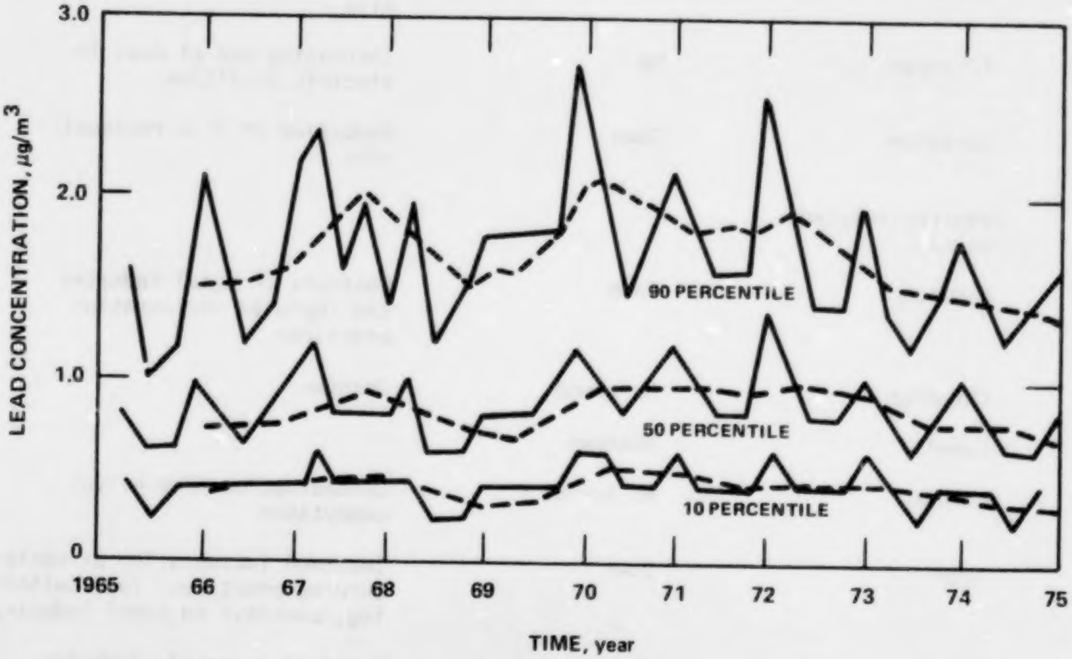


Figure 5-41. Seasonal patterns and trends in quarterly average urban lead concentrations.

Source: Faoro and McMullen, 1977.

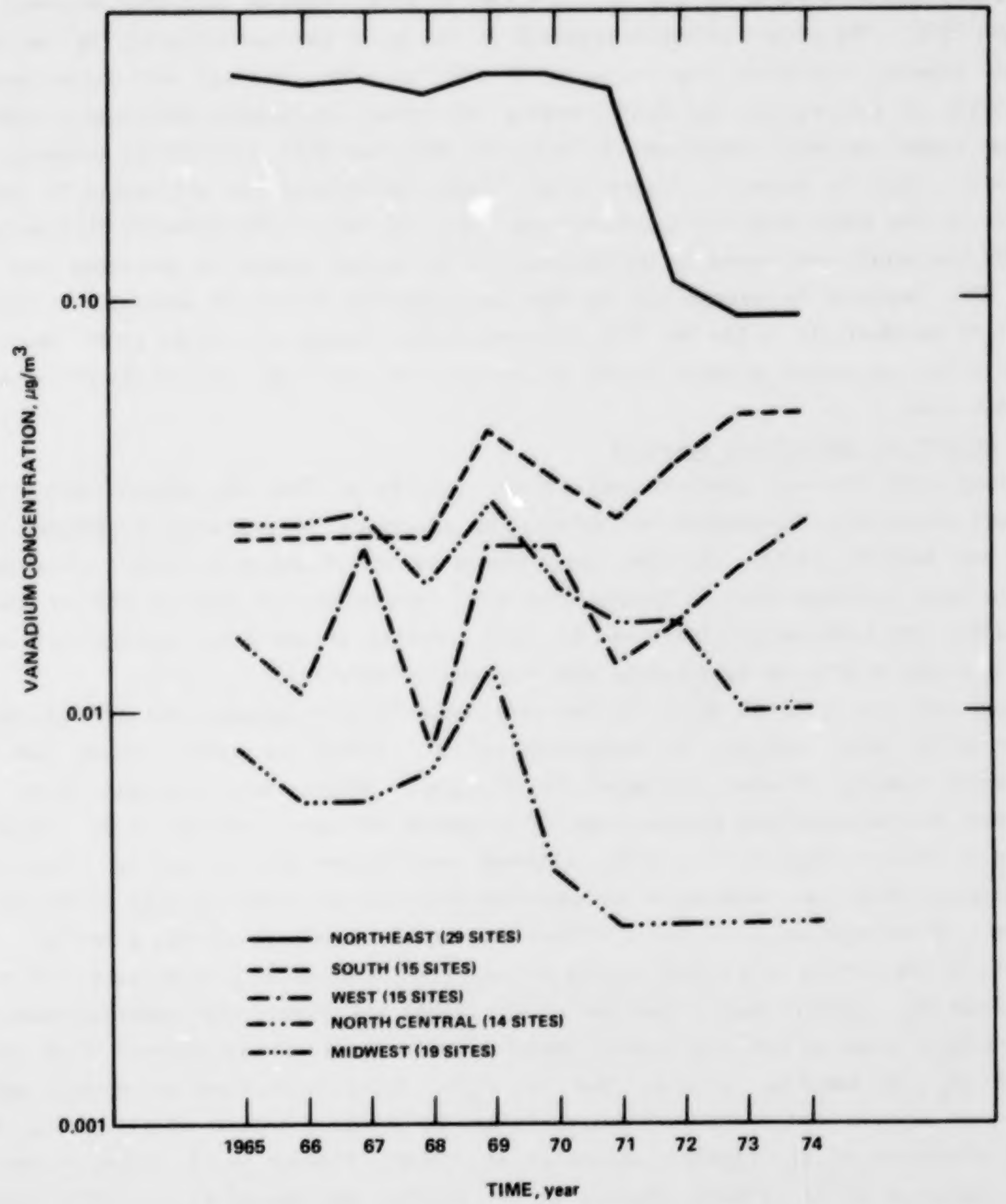


Figure 5-42. Regional trends in the 90th percentile of the annual averages for vanadium. (Δ indicates value below lower discrimination limit.)

Note: 1971-1974 90th percentile below lower discrimination limit of 0.003 = $\mu g/m^3$ in the midwest.

Source: Faoro and McMullen (1977).

74 percent, from 0.35 $\mu g/m^3$ in 1969 to 0.09 $\mu g/m^3$ in 1974. Most of this drop occurred between 1971 and 1972. The slight increase apparent in the South was caused mainly by two or three stations showing relatively high readings in 1972 to 1974; this was not characteristic of other sites in the region. For both vanadium and nickel, pronounced and regular high winter and low summer seasonal variations in both the 50th and 90th percentiles occurred in the Northeast. This is shown in Figure 5-43. These variations are attributed to the metal contents in the fuels used for space heating. The decrease in the 50th and 90th percentiles of these two metals was caused by the decrease in the sulfur content in petroleum used in this area. This decrease is exemplified by the approximately 70-percent decrease in the sulfur content of residual oil in the New York City-Westchester County area since 1979. The vanadium concentrations decreased between 70 and 80 percent over the same time period at the New York City NASN site.

5.5.5 Acidity of Atmospheric Aerosols

Along with size and chemical composition, acidity of fine atmospheric aerosols is an important property. Measurement of acidity by titration is preferred to pH measurements (Junge and Scheich, 1971). To date, measurements of the strong acid content of atmospheric aerosols have indicated that it is quite variable. Around certain sources such as cement and lime kilns, the airborne particles may be basic, whereas around other sources such as H_2SO_4 plants and coke plants the particulate emissions may be very acid.

Weak and strong acids exist in the atmosphere in both gaseous and particulate form. Organic acids were reported by Ketseridis et al. (1976) in rural, urban, and marine atmospheres ranging between 0.3 $\mu g/m^3$ to 10 $\mu g/m^3$. Nitric acid has been found in the atmosphere in concentrations ranging from < 2 to nearly 100 $\mu g/m^3$ (Spicer, 1977). Vapor-phase HCl may be present (Rahn et al., 1979), although quantitative data are sparse. These organic and inorganic gases can condense or be adsorbed on particles either _in situ_ or during filter sampling. As pointed out previously, filters are capable of absorbing HNO_3 directly.

Most of the strong acid found in aerosol particles is chemically associated with the fine particulate SO_4^{2-} aerosol mass. Charlson et al. (1978) and others cited numerous measurements of approximate chemical balance between ammonium cations and sulfate anions. Thus the major form of SO_4^{2-} is ammonium sulfate (that is, H_2SO_4 fully neutralized by ambient ammonia). However, on occasion urban and rural aerosols can be acidic. Brosset et al (1975), Brosset (1978), Hitchcock et al. (1980), Cobourn et al. (1978), Pierson et al. (1980), Lioy et al. (1980), Leaderer et al. (1982), Stevens et al. (1979), and Tanner et al. (1977, 1979) all demonstrated that strong acid in the form of NH_4HSO_4 and, less frequently, H_2SO_4, may exist at significant levels in the ambient atmosphere. Strong acid levels equivalent to > 15 $\mu g/m^3$ of H_2SO_4 have been observed for periods ≥ 6 hours.

In urban atmospheres, sulfate anion usually appears primarily in the form of ammonium sulfate or ammonium bisulfate (NH_4^+/SO_4^{2-} molar ratios between 1 and 2) as reported by Lioy

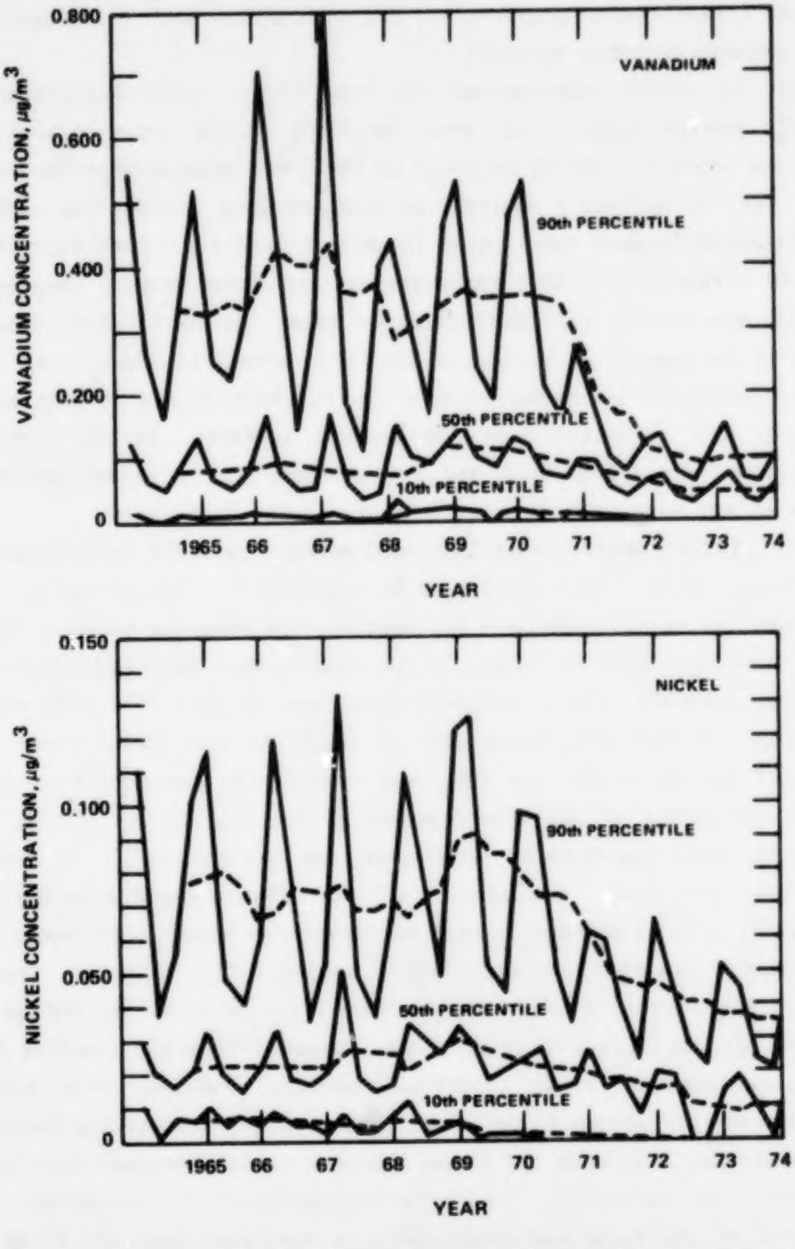


Figure 5-43. Seasonal variation in quarterly averages for nickel and vanadium at urban sites in the northeast.

Source: Faoro and McMullen (1977).

et al. (1980) for New York City, Leaderer et al. (1982) for New Haven and New York City, and Cobourn et al. (1978) for St. Louis. Presumably this greater extent of neutralization of urban SO_4^{2-} aerosols is due to additional NH_3 sources in urban areas, although it may be due in part to analytical interferences from coarse, basic particles such as resuspended cement dust present in large amounts in urban aerosols.

On the basis of recent experimental and theoretical work, Huntzicker et al. (1980) indicate that SO_4^{2-} aerosol more acidic than $(NH_4)HSO_4$ should occur only when SO_2 is being oxidized rapidly and where the ratios of $[SO_2]$ to $[NH_3]$ are high or when the equilibrium vapor pressure of NH_3 over the partially neutralized H_2SO_4 droplet exceeds the ambient NH_3 partial pressure. The situation is more complicated in ambient aerosols in which partially ammoniated SO_4^{2-} is present in mixtures with NO_3^-, carbonaceous, and other aerosol components in solid or liquid form which may affect its neutralization rate. In particular, some data (Tanner, 1980a) suggest that the degree of mixing in the "well-mixed" boundary layer is inadequate to prevent vertical stratification of strong acid levels since NH_3 is largely emitted (and HNO_3 largely removed by dry deposition) at the earth's surface. Further information on the vertical distribution of strong acid and related species is needed before emission and neutralization rates may be used to predict acid levels in urban areas.

Cobourn et al. (1978) demonstrated that acid aerosol episodes could occur in urban areas as suggested by Tanner et al. (1977, 1979) and Brosset (1978). Cobourn et al. (1978), using a continuous SO_4^{2-} monitor to distinguish H_2SO_4 species from ammonium sulfate, recorded two acid aerosol episodes lasting 3 days or longer in St. Louis, MO. Both episodes were reported to have occurred simultaneously with a regional haze, one in July 1977, the other in February 1978. Cobourn ascribed the city occurrence of H_2SO_4 to conditions where atmospheric NH_3 concentrations were exceptionally low (NH_3 was temporarily depleted from the atmosphere).

The temporal variations of the acid fraction of the SO_4^{2-} aerosol in St. Louis displayed patterns similar to those reported by Cunningham and Johnson (1976) in Chicago and Tanner (1980b) for the New York area. The aerosol acidity often changed drastically within a few hours. Cobourn et al. (1978) noted a diurnal pattern with highest acid levels in midafternoon and lowest at night. Leaderer et al. (1982), taking 6-hour samples, reported increased aerosol acidity in the noon to 6 p.m. samples taken at High Point, NJ and Upton, Long Island (west and east of New York City, respectively), compared to other sampling times. At this time the relative contribution of SO_2 oxidation chemistry, temporal variations in NH_3 and SO_2 emission rates, diurnal variations in turbulent mixing rates, and varying height of the mixing layer to the diurnal patterns were not known. Dzubay (1980) observed that while sulfur and lead dominated the fine particles, they were insignificant in the coarse particles. The similar composition of the rural and urban aerosols indicated that the urban materials were transported to the rural areas.

Measurements of acidity in eastern United States aerosol samples indicate that strong acids are present more frequently and in larger amounts in rural and semirural samples than in the urban samples. Pierson et al. (1980) reported 12-hour concentrations of H^+ ions expressed as H_2SO_4 as high as 17 µg/m^3 in the Allegheny Mountains of Pennsylvania in July and August 1977. It is likely that strong acid concentrations were substantially higher for periods less than 12 hours.

Lioy et al. (1980) and Leaderer et al. (1982) characterized the aerosol acidity in the region surrounding New York City during the summer of 1977. The samples taken at High Point, NJ (west-northwest of the city), were more acidic (17.8 µg/m^3, 6-hour average maximum H^+ ions expressed as H_2SO_4) than samples taken in New Haven, CT, and Brookhaven, Long Island, NY.

Part of the period studied by Lioy et al. (1980) was coincident with the research of Pierson et al. (1980). Using the combined data set in conjunction with air parcel trajectories and haze analyses, Lioy et al. (1980) suggested the presence of a regional acidic aerosol distribution encompassing an area at least 200 miles in diameter during the period August 3 to 9, 1977.

As pointed out earlier, atmospheric particles are nearly neutral for the most part, presumably because of the presence of NH_3 in the atmosphere. However, instances of particulate acidity have been reported in several credible studies done in the East, in both winter and summer and in rural and urban sites.

5.6 COARSE PARTICLES IN AIR

5.6.1 Introduction

In Chapter 2 and in earlier sections of this chapter it was shown that air in cities usually contains large amounts of particles larger than 1 to 3 µm in size. Particles larger than 10 to 20 µm tend to settle out of air suspension under the force of gravity. Yet in many areas these very large dust particles are also present in substantial quantity. This material is quite commonly deposited as dust on window ledges and silt on roadways. For potential effects of the ambient concentrations described below, the reader is directed to Chapter 10, Section 10.3.2, for descriptions of soiling and to Chapter 11, Section 11.2, for information on deposition of particles in human airways. Coarse-particle mass contributions are substantial and important in the context of air pollution effects.

The composition and sources of coarse particles are not as thoroughly studied as those of fine particles. One reason is that they are more complex. For example, it is possible to recognize dozens of particle types in ambient air samples; these range from soil particles, limestone road aggregate, fly ash and oil soot to cooking oil droplets, pollen, wood ashes, and even instant coffee (McCrone, 1968; Draftz and Severin, 1980). Man's industry and activity stirs up dust, quite a lot of dust in arid climates. Unfortunately, the chemical composition of many kinds of coarse particles can be very similar, at least as determined by elemental analysis. Consequently, much of the evidence on large-particle composition has been obtained from deductions based on microscopical examination.

5.6.2 Elemental Analysis of Coarse Particles

Measurable elements constituting the major portion of coarse-particle mass in cities are silicon, aluminum, calcium, and iron (Akselsson et al., 1975; Lewis and Macias, 1980; Camp et al., 1978; Stevens et al., 1980; Dzubay, 1980; Stevens et al., 1978; Cahill et al., 1977; Hardy, 1979; Trijonis et al., 1980). Although these elements do exist in the fine fraction to a minor degree, they are everywhere substantially enriched in the coarse fraction.

Occurrence of some elements in coarse particles is time and place dependent, though, and Table 5-20 shows some data illustrative of this point. There appear to be substantial differences across the country in the fraction of these elements occurring in coarse particles. The presence of local sources dominates both the mass and composition of coarse particles. However, Cooper and Watson (1980) have graphically demonstrated the similarity in elemental distribution for a variety of coarse-particle sources as Figure 5-44 shows. Here, the most that can be said is that rock-grinding operations produce remarkably similar coarse-particle elemental compositions, whether the mechanical action is intentional or incidental to other activities. Cement dust and limestones (not surprisingly) also have similar elemental composition (Draftz, 1979).

Even greater evidence of localized influence on coarse-particle concentrations can be seen with other elements. In the Smoky Mountains, titanium and chlorine are greatly enriched in the coarse particles (Stevens et al., 1980) while in St. Louis, titanium is mainly a fine-particle component and chlorine is about evenly distributed between coarse and fine particles (Stevens et al., 1978; Akselsson et al., 1975). In the case of titanium, the emissions from a paint plant greatly influence the fine-particle titanium (Rheingrover, 1981). Chlorine appears to originate in fine automotive particles at inland sites (Winchester et al., 1967) but in coarse sea-salt particles near the coast (Hardy, 1979; Draftz, 1979).

A variety of carbon-containing species, particularly organics and carbonates, sometimes can be found in substantial quantities in coarse particles. For example, De Wiest (1978) found 30 to 50 percent of extractable organics in 2 to 10 μm particles. Lewis and Macias (1980) found 40 percent of the carbon (presumably mostly in organic compounds) in dichotomous sampler coarse fractions in Charleston, WV, while Stevens et al. (1980) found about one-third of the organic compound mass in the coarse fraction in the Great Smoky Mountains. Mueller et al. (1970) were able to differentiate between carbonates and elemental carbon by acid evolution of CO_2, but this technique, unfortunately, has not been applied to coarse-particle analysis. Considering that calcium carbonate has often been found as a major component of urban coarse-particle samples (Graf et al., 1977; Draftz, 1979), it is surprising that direct analyses for carbonate have not been reported. Elemental carbon appears to be uncommon in coarse particles. As mentioned previously, most water-soluble inorganic ions are found in fine fractions.

TABLE 5-20. COARSE PARTICLE SILICON, ALUMINUM, CALCIUM, AND IRON

		μg/m^3					Coarse/fine mass ratios				
Location	Dates	Coarse mass	Si	Al	Ca	Fe	Si	Al	Ca	Fe	Reference
Charleston, WV	08/25-9/14/76	27.1	2.8	1.1	0.96	0.59	6.8	15	9.7	4	Lewis and Macias, 1980
	05/11-05/19/77	43	7.7	NA	2.2	1.4	7	NA	7.4	4	Camp et al., 1978
Smoky Mountains, TN	09/21-09/26/78	5.6	0.50	0.20	0.32	0.12	15	10	20	4	Stevens et al., 1980
New York, NY	02/77	42.6	2.0	0.84	1.15	0.96	5.6	6.5	3.2	2.5	Stevens et al., 1978
Philadelphia, PA	03/77	17.5	1.8	0.64	0.94	0.69	7	13	6	3.2	Stevens et al., 1978
St Louis, MO	12/75	NA	4.3	8.7	1.9	1.0	10	4.4	16	3	Stevens et al., 1978
Portland, OR	02/77	27.6	2.8	1.2	0.76	0.95	31	5.6	11	5.0	Stevens et al., 1978
Glendora, CA	03/77	NA	1.0	0.3	0.44	0.36	5.3	>6	4.5	3	Stevens et al., 1978
St. Louis, MO	08/-09/76	28.0	4.5	1.2	2.8	1.2	10	6	21	4.4	Dzubay, 1980

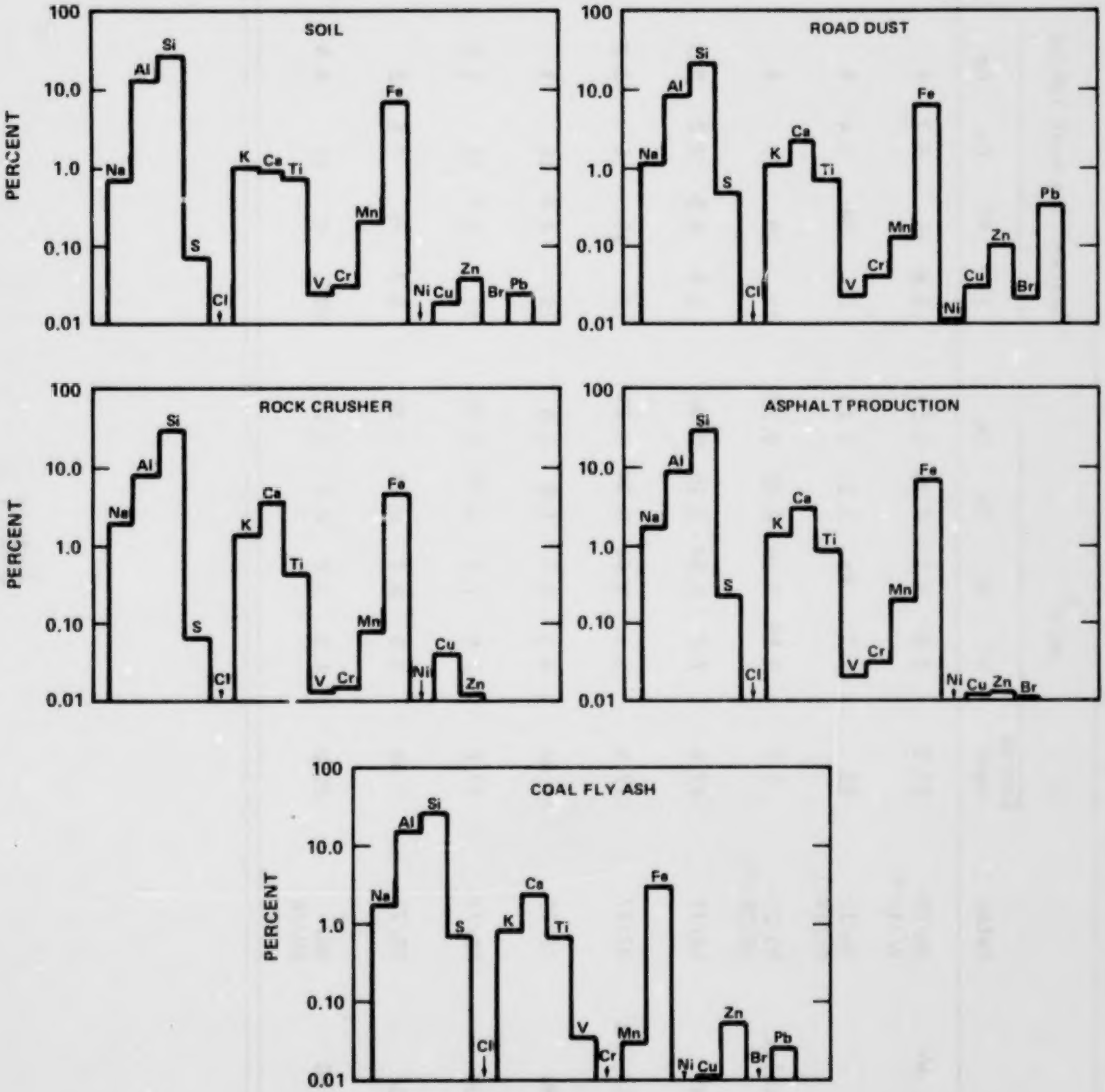


Figure 5-44. Elemental composition of some coarse particle components.

Source: Cooper and Watson (1980).

5.6.3 Evidence from Microscopical Evaluation of Coarse Particles

Efforts to understand the importance of coarse particles in air have been hampered by the inability of simple chemical analyses (so very successful with fine particles) to reveal much of their nature. However, estimates of mass balances have suggested for a long time that locally generated coarse particles must constitute a substantial part of the suspended particle burden.

As an example, the most recent data from the EPA network of dichotomous samplers and hi-vols could be interpreted as demonstrating significant amounts of particles larger than 15 µm in the air, if the difference between the dichotomous sampler total and TSP is taken as representing supercoarse particles. Table 5-21 displays some of these data for selected sites for illustrative purposes. Most sites have two-thirds or more of the TSP in coarse and supercoarse particles. For the more arid and dusty parts of the country, rough estimates of this kind and common sense have suggested to pollution control officials that TSP must be dominated by locally generated coarse particles.

Since these larger objects can be readily inspected with an optical microscope, a substantial body of information has been accumulated by visually inspecting particle samples, such as hi-vol filters or impactor stages. The largest of these studies involved evaluation of 300 filters from 14 U.S. cities (Bradway and Record, 1976). Table 5-22 presents composite analyses for all filters from each of the cities. A wide variation was found in these filters ranging from virtually all dust in Denver and Oklahoma City to mostly dust with considerable fly ash and soot in most of the industrialized cities. Chattanooga was anomalous, in that extremely large amounts of plant materials were found, including pollen, fibers, fragments of leaves, and other tissues.

Similar investigations were combined with emissions inventory, modeling, and control studies in Phoenix, AZ, in 1977 (Richard, 1977; Richard and Tan, 1977; Richard et al., 1977a,b; Graf et al., 1977). In that city, 90 percent of the TSP was found to be mineral dust apparently entrained in air by automotive traffic over 1100 miles of unpaved roads in the area and by intense construction activities. Suck et al. (1978, 1979) found, through meteorological modeling, that very little motion of this coarse PM occurs in the wind. Since wind velocities are characteristically low, agricultural influences are minor and coarse particles stay more or less where they are generated.

Microscopic evaluations of Miami and St. Louis particles have been conducted both on total filter samples and on impactor plates (Draftz, 1979; Draftz and Severin, 1980). In Miami, calcite (calcium carbonate) was the principal component of the coarse particles. There was evidence that a small part of the calcite was recrystallized from ocean spray. However, most of the calcite appeared to be roadway aggregate suspended in the air. There were also significant quantities of halite (NaCl) and other trace elements characteristic of sea salt.

TABLE 5-21. RELATIVE AMOUNTS OF FINE, COARSE, AND SUPERCOARSE PARTICLES AT SELECTED SITES

	Weight percent		
	Fine <2.5 μm	Coarse 2.5<cut>15μm	Supercoarse >15μm
Phoenix, AZ	34	6	60
El Paso, TX	16	51	33
Dallas, TX	26	10	64
Portland, OR	32	64	4
Los Angeles, CA	36	31	33
Akron OH	49	26	25
Philadelphia, PA	51	32	17
Hartford, CN	34	32	34

Note: The term supercoarse refers to the difference between the hi-vol TSP concentration and total dichotomous sampler concentration.

Source: U.S. Environmental Protection Agency (1981).

TABLE 5-22. FOURTEEN-CITY STUDY - MICROSCOPICAL IDENTIFICATION OF COARSE PARTICLES COLLECTED IN URBAN ATMOSPHERES

	Wt. % of Component			
Location	Minerals	Combustion products	Biological material	Miscellaneous (rubber tire debris)
Oklahoma City	88	8	1	4
Denver	81	7	1	11
Miami	79	9	1	12
St. Louis	75	21	>1	4
Washington, DC	70	23	5	2
Baltimore	69	25	3	3
Birmingham	66	22	2	10
Philadelphia	64	33	1	2
Providence	64	22	1	13
Seattle	60	27	3	10
San Francisco	52	29	3	16
Cincinnati	51	44	1	4
Cleveland	51	40	1	8
Chattanooga	36	35	16	13

Source: Bradway and Record (1976).

The general picture from these studies is that coarse particles are contributed from numerous local sources and vary dramatically from place to place. It is likely that dust and roadway aggregate suspended by traffic are major sources of coarse particles. However, in in industrialized cities especially, there is still some evidence of combustion source contributions.

5.6.4 Fugitive Dust

In the discussion of coarse particles, evidence was presented that a substantial portion of TSP, usually more than half, is accounted for by coarse or supercoarse particles, and a great portion of this mass is mineral dust, also called "crustal material" in many of the papers reporting chemical analytical data. There is growing opinion that this major component of TSP is contributed almost entirely by agitation of soil in some way, and this component is commonly called fugitive dust. One of the major sources for fugitive dust generation is vehicle traffic; the motion of vehicles can reentrain silt (fine soil particles) that has been deposited by settling from the air, washing from nearby areas in rain, or falling from vehicle tires. All these mechanisms were significant in the Phoenix, AZ, study cited previously (Richard, 1977; Richard and Tan, 1977; Richard et al., 1977a,b). These emission sources and related ones are discussed in some detail in Chapter 4.

In an assessment of particle source influence on TSP in western States, reentrained dust from paved and unpaved roads accounted for 10 to 75 percent of TSP emissions and 16 to 49 percent of TSP concentrations at critical receptor locations in 20 inland western cities (Axetell, 1980). In most of these locations, 40 to 60 percent of TSP emissions were from roadways. One critical feature of this observation, apparently mainly derived from microinventory studies around TSP monitors, was the traffic volume on unpaved roads. Cowherd et al. (1979) reported emission factors from unpaved roads of about 300 grams/vehicle-km traveled. Consequently, even rather small traffic volumes can generate substantial TSP contributions. There are very large State-to-State variations in both the remaining number and length of unpaved roads and the traffic volume such roadways carry. Carpenter and Weant (1978) analyzed the available information on roadway use and found that while unpaved roads were fairly common in the western mountains, deserts, and Great Plains, other areas of the country, the Southeast and New England especially, also had many miles of unpaved roads and substantial roadway contributions to TSP. In industrial areas, truck traffic over access roads can be a major source of TSP emissions (Cowherd et al., 1979).

The wind alone can be a major source when velocities are high and the soil aggregates are small. For example, Gillette (1978) estimated soil fluxes for six test soils in a wind tunnel. He concluded that windspeed and crust play major roles in wind entrainment. A surface crust effectively eliminated fine-particle entrainment and greatly reduced coarse particle entrainment.

Wilson et al. (1979) found that car and truck traffic produced large amounts of dust on unpaved mining roads in northeastern Minnesota. Particle sizes were mainly in the 6 to 30 μm range near the roadway, but large particles were found at about one-fifth the roadside level 400 or 500 meters downwind. There was visual evidence of dust coating roadside foliage and gusts of wind caused major short-term pulses in particle concentrations downwind of the road. Davidson and Friedlander (1978) measured deposition of coarse particles on Avena, the common wild-oat grass of the Far West. Dry deposition on the stems of such plants was reported to be a significant removal mechanism for particles larger than about 7 μm.

Reentrainment of road dust has been found a major source of coarse particles in central business districts. In a study of several sites in Philadelphia, Record and Bradway (1978) concluded that entrainment of dust from roadways contributed the majority of street-level coarse particles and very significant levels at rooftops, 11 meters above the street. Rainfall, if there was enough of it, reduced the dust levels significantly (e.g., about 20 percent). However, attempts to flush the street with water redistributed the fine particles and increased the observed coarse-particle level.

In a study of one site in Massachusetts, Record et al. (1979) found coarse-particle levels highly correlated with traffic volume as shown in Figure 5-45. In this study, very large contributions of roadway salt, used for winter snow control, were found in the coarse particles.

Yocom et al. (1981) estimated, by analysis of a variety of records, the contribution of fugitive dust to areawide particle burdens in Allegheny County, PA. They found both industrial sources and roadways to be significant contributors, though in widely varying proportions. In the 12 study sites, roadway dust contributed from a low of 4 percent to a high of 45 percent of annual geometric mean TSP. In most sites, 15 to 20 percent of these particles came from traffic. Industrial fugitive particle emissions were more significant in this area, although the general range was similar, 5 to 40 percent of the annual level. In most sites, industrial fugitive dust contributed 20 to 30 percent of the TSP and was greater than roadway dust. These two sources, together with the general area background, accounted for 80 to 90 percent of the TSP burden in Allegheny County.

Clearly, fugitive dust is a major contributor to TSP in most U.S. monitoring sites. There is evidence that unpaved roadways and commercial streets can be major sources. Since reentrained dust appears to be mainly coarse mode particles, monitor-siting considerations, and especially monitor height or slant distance relative to roadways, can markedly alter the observed TSP level (Pace et al., 1977; Record et al., 1979).

How important this fugitive dust might be in assessing exposure relative to potential effects is not clear. Of those cited in this section, only the Record et al. (1979) study reported particle size data; further, the whole issue of the relationship of outdoor concentrations to exposures is under serious question. (Vide infra, §5.8)

It is also interesting to note in Table 5-22 that there is always some PM of biological origin in atmospheric particles. Occasionally, especially during pollen season, this material can account for a significant fraction of the coarse-particle mass (Draftz et al., 1980).

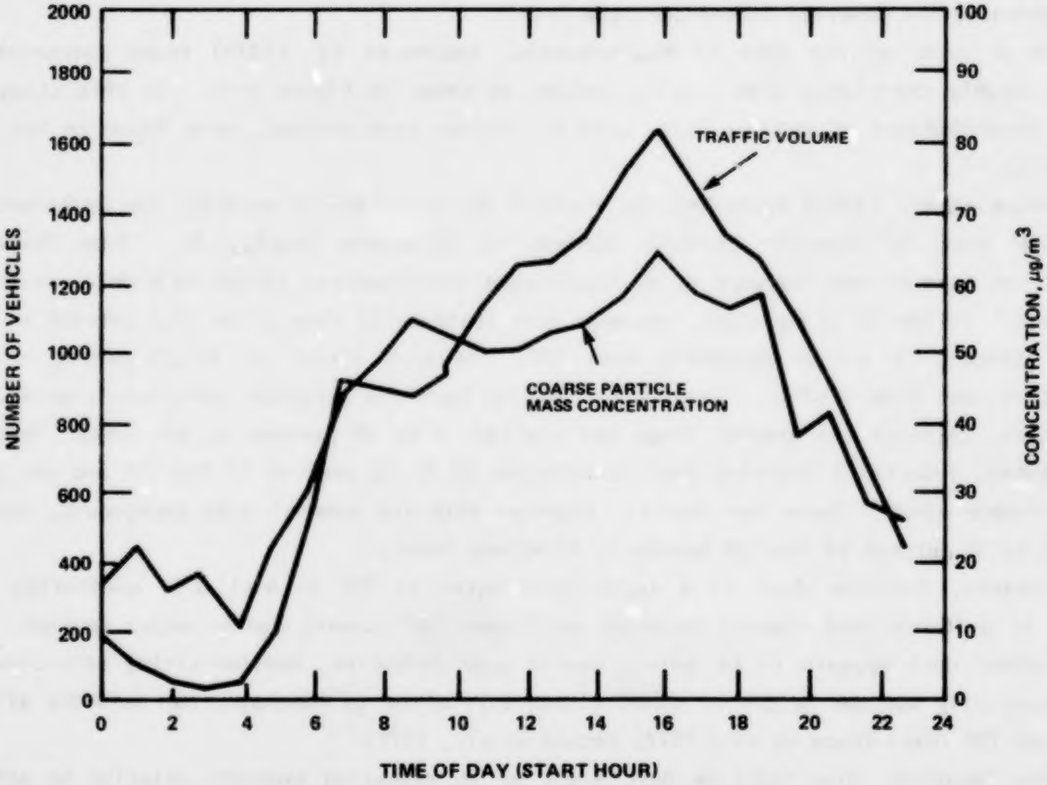


Figure 5-45. Diurnal variation of particle concentrations and Plymouth Avenue traffic volume in Fall River, Mass., during March through June 1979 (weekdays only), shows contribution from reentrained particles.

Source: Record et al. (1979').

Draftz et al. (1980) also identified cornstarch as a major contributor to particle mass in some nonattainment areas. These authors also found a few other reproductive stages of organisms such as conidia spores. It has been hypothesized that bacteria occur in coarse aerosols, perhaps even legionella pneumophilia (Fraser and McDade, 1979). However, the presence of airborne infectious organisms has usually been deduced by disease incidence rather than by direct measurement, and quantitative techniques are largely lacking. Considering the importance of viable particles in allergies, for example, this area could be a desirable one for future research.

5.6.5 Summary

The wind, traffic, construction, mining, and general industrial activity are the major causes of coarse particles suspended in the air. Dry climates, intense construction activity, lack of paving, and salt from icy streets or the sea can all be contributing factors. The quantitative assignment of particular sources to the coarse and fine particle burdens has been addressed in a cursory and introductory fashion in this section. In the next part, more formal systems for this source apportionment will be addressed.

5.7 SOURCE-APPORTIONMENT OR SOURCE-RECEPTOR MODELS

For quite a long time, the goal of quantitatively determining the contributions of particle sources to ambient PM concentrations has been pursued. Recently, Cooper and Watson (1980) and Gordon (1980) reviewed the current status of calculational systems or models to estimate source contributions to atmospheric particle concentrations. Cooper and Watson described several methods in a systematic sense, and Figure 5-46 shows their analysis of models capable of yielding at least semi-quantitative information. Many microscope-based conclusions were discussed in the previous section and the work of Yocom (1981) is basically an example of series analysis. However, chemical mass balance and multivariate models have been used quite effectively recently and a few examples of these approaches are cited below. The results from three cities (St. Louis, MO, Denver, CO, and Portland, OR) illustrate the contrast in fractional contributions of PM from different sources.

In analyzing the St. Louis Regional Air Pollution Study (RAPS) dichotomous sampler data by x-ray fluorescence, Dzubay and Stevens (1975) found 75 percent of the zinc, sulfur, bromine, arsenic, selenium, and lead occurred in the fine particles and at least 75 percent of the silicon, calcium, titanium, and iron in the coarse fraction. Using groupings of elements to represent sources, Dzubay (1980) postulated the sources making fractional contributions to 2-month summer mean concentrations at several sampling locations in St. Louis. Approximately 50 to 70 percent of the concentration of fine particles was made up of ammonium sulfates. The next largest identifiable source was motor vehicle emissions, followed by shale and other sources.

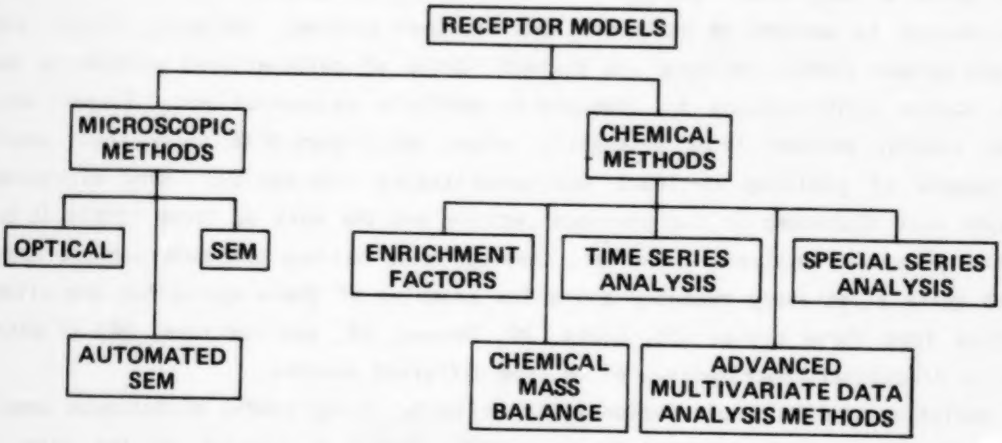

RECEPTOR MODELS
MICROSCOPIC METHODS
CHEMICAL METHODS
OPTICAL
SEM
AUTOMATED SEM
ENRICHMENT FACTORS
TIME SERIES ANALYSIS
SPECIAL SERIES ANALYSIS
CHEMICAL MASS BALANCE
ADVANCED MULTIVARIATE DATA ANALYSIS METHODS

Figure 5-46. Types of receptor source apportionment models.

Source: Cooper and Watson (1980).

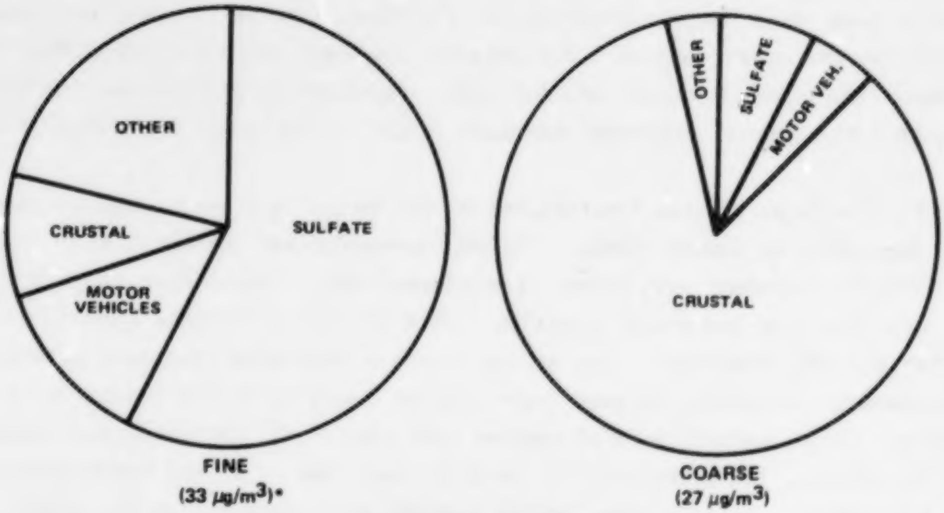
Pace and Meyer (1979) resolved the constituents found in the St.Louis dichotomous sampler data to demonstrate the relative contributions of sources to the urban and nonurban concentrations (see Figure 5-47). As might be expected, the vehicle emission component was much smaller in the rural samples than it was in the urban samples. The SO_4^{2-} fraction in the nonurban sites made up a larger proportion of the total fine particulate mass than did the SO_4^{2-} fraction in the urban samples. The crustal component and the nondescribed components remained about the same in both sets of data. Looking at the coarse fraction, it is interesting that the crustal component was much larger in the urban sites than it was in the nonurban sites.

The monthly averages of size fractionated Denver aerosol mass were compared for 2 months, January and May 1979, by Dzubay (1980). The SO_4^{2-} component was smaller than in St. Louis and the motor vehicle component was larger (see Figure 5-48). The winter concentrations were higher for both the fine and coarse fraction. Much of this difference appeared to be in the excess carbon and NO_3^- component. The coarse fraction contained road salt particles in the winter. Presumably, accompanying sand could account for part of the unidentified mass. In Denver samples, unlike eastern aerosol samples, the summer SO_4^{2-} concentrations appeared to be lower than in winter. The asterisks (*) indicate that some or all of the component could be due to excess carbon. In this case "excess carbon" was determined by the amount of carbon observed less the amount accounted for by the identified sources. In the winter, the carbon concentration in the fine fraction was 17 $\mu g/m^3$. It was not determined for the coarse fraction. In May, the unfractionated carbon was 7.2 $\mu g/m^3$. Wood burning and vehicle exhaust are believed to be the important carbon sources in Denver.

Chemical element balance techniques were applied to TSP and fine-fraction aerosols collected in Portland, OR, in a year-long study. Cooper et al. (1979) describe the experiment and results. Figure 5-49 summarized the resulting source allocation. As in several other findings, soils and road dust were important components of TSP. The study revealed that burning vegetation was the second most important source, contributing almost 15 percent of the TSP mass and 20 percent of the fine-particle mass. Sulfate was not the most abundant component of the fine-particle mass. In fact, it was only 8 percent of the mass, fourth after auto exhaust, volatilizable carbon, and aerosols from vegetation burning. The study showed the contribution of residential wood burning to ambient aerosol concentrations.

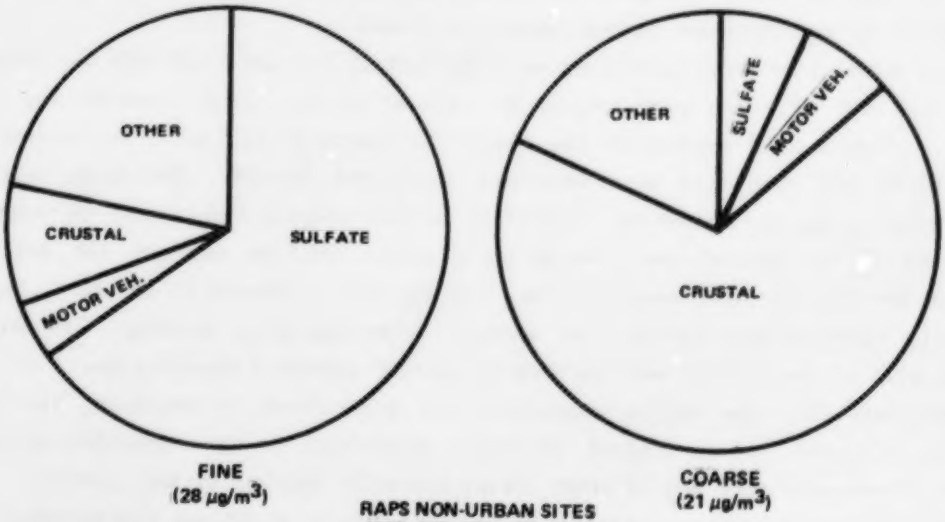
Studies resolving the source components are great aids in resolving the fractional contribution of local versus distant sources. Resolution of this question may await the application of receptor modeling to other cities and other regions of the country.

Source-receptor techniques, which rely on measurements of PM and composition, can often be combined with studies of wind direction or of synoptic air mass motion to further elucidate source effects on ground pollutant levels. For example, Rodhe et al. (1972) studied the soot and SO_4^{2-} concentrations at four coastal sites in Sweden. By combining wind direction data



RAPS URBAN SITES
(103, 105, 106, 108, 112)

*2-MONTH AVERAGE CONCENTRATIONS



RAPS NON-URBAN SITES
(115, 118, 120, 122, 124)

Figure 5-47. Source contributions at RAPS sites for July-August 1976 estimated by chemical element balance.

Source: Pace and Meyer (1979).

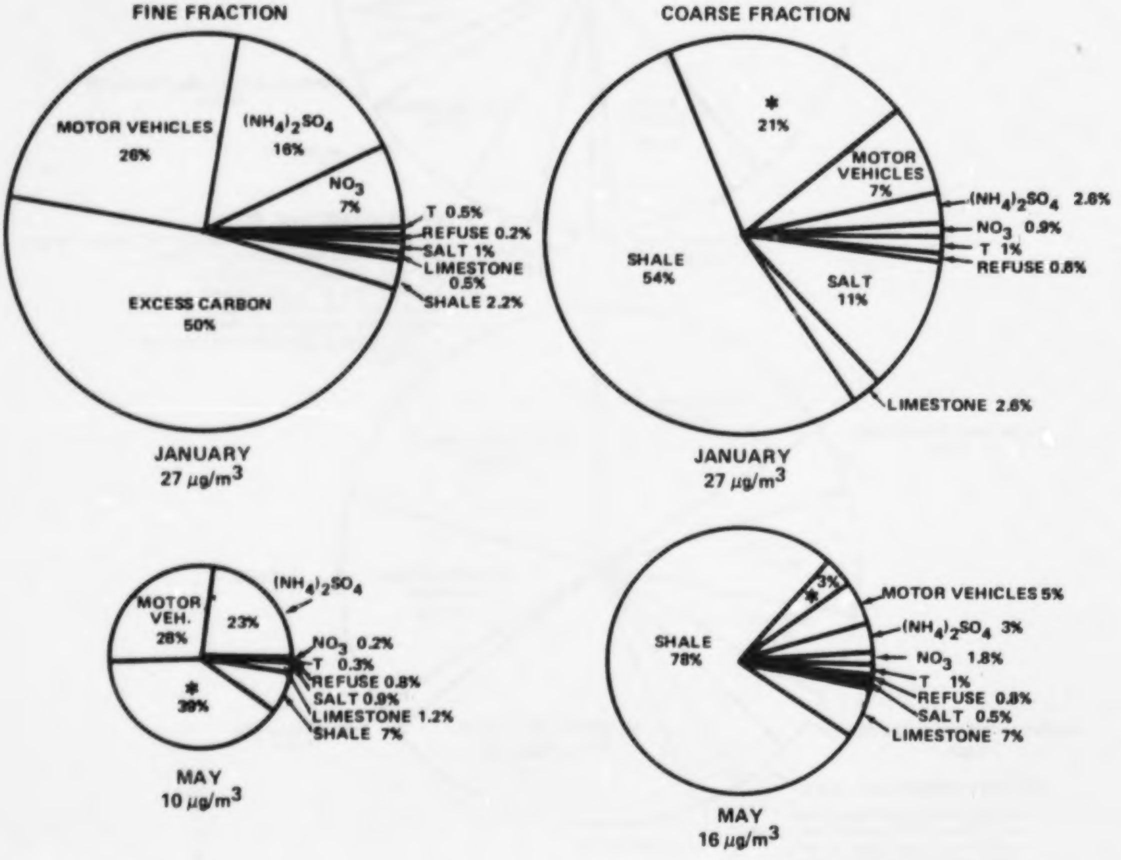


Figure 5-48. Monthly averages of size fractionated Denver aerosol mass and composition for January and May, 1979.

Source: Dzubay et al. (1981).

***Some or all of component possibly due to excess carbon.**

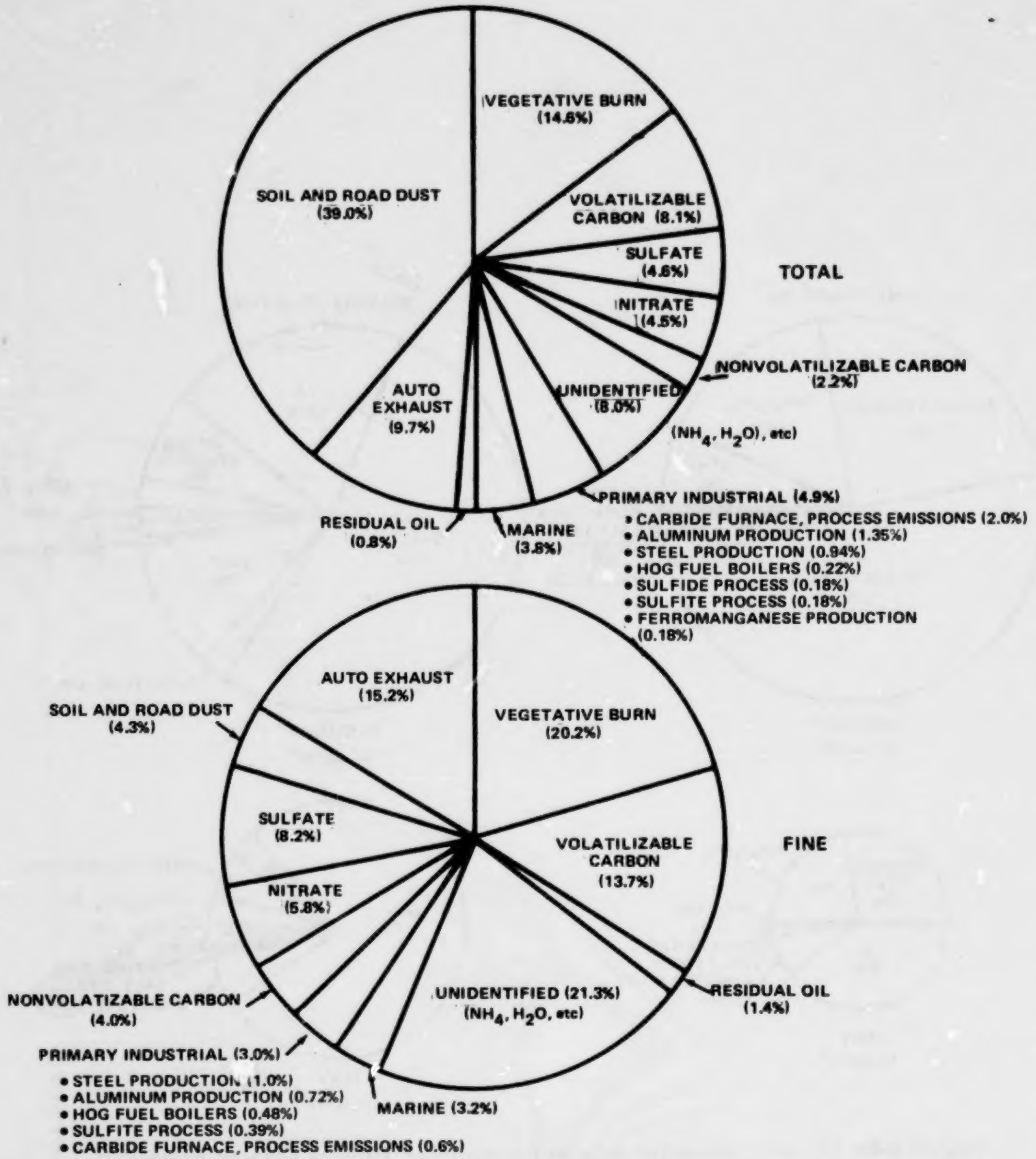


Figure 5-49. Aerosol source in downtown Portland, annual stratified arithmetic average. Does not include the 17%, on the average, of material collected with the standard hi-vol sampler which was not collected and characterized with the ERT-TSP sampler. Volatilizable and non-volatilizable carbon are operational definitions which approximately correspond to organic and elemental carbon, respectively.

Source: Cooper et al. (1979a).

with observations of high SO_4^{2-} and soot loadings, these authors deduced the existence of long-range transport of air pollutants from industrialized areas of northern Europe. Trijonis (1980) used similar analysis in detailing local source contributions to PM at specific monitoring sites in St. Louis.

Samson (1981) developed a more elaborate model based mainly on the trajectory analysis procedure of Heffter et al. (1975). This model was used to plot area source contributions to ground-level SO_4^{2-} values reported in the literature for seven rural sites in the northeastern United States. Samson concluded that high concentrations of sulfates appear to be consistently associated with upstream (upwind) stagnation. Further he found that incorporation of the magnitude of SO_2 emissions and the upstream mixing height into the model did not improve the correlation between measured SO_4^{2-} and upwind stagnation as estimated by the inverse of windspeed.

This class of models appears to offer some promise for future applications, but like the somewhat more complex Lagrangian trajectory models discussed in Chapter 6, it has some problems. Samson (1981) pointed out that a complete investigation of sulfur budget (or that for any other pollutant, for that matter) would require measurements of the vertical profiles of pollutants over a very wide area. Clearly, these data requirements are not likely to be met by experiments in the near future. The reader is directed to Chapter 6 for further discussion of deterministic models and their data requirements, successes, and shortcomings.

5.8 FACTORS INFLUENCING EXPOSURE

5.8.1 Introduction

To this point only outdoor concentrations of SO_2 and PM have been considered in the present discussion. Outdoor concentrations are of major concern in estimating air pollution effects on visibility, and ecological and materials damage. However, people spend the majority of their time inside buildings or other enclosures; they breathe mostly indoor air and, therefore, indoor concentrations dominate average exposure. To the extent that indoor concentrations are different from the outdoors, population exposures are different from those estimated by outdoor monitors.

In the United States the population is highly mobile. Many persons in their daily travel pass through areas of both high and low pollution levels within a city. Others work or play outdoors to a greater degree than the general population. Therefore, individual exposures to SO_2 and PM vary more widely than measurements from stationary outdoor monitors suggest (Spengler et al., 1979).

Furthermore, individual variations in respiratory anatomy, illness, or smoking habits can exert important influences on the dose of a pollutant retained by individuals receiving the same exposure. For example, Cohen et al. (1979) found that smokers retain test particles longer than nonsmokers. Figure 5-50 presents the results of a study of 12 subjects, 3 of

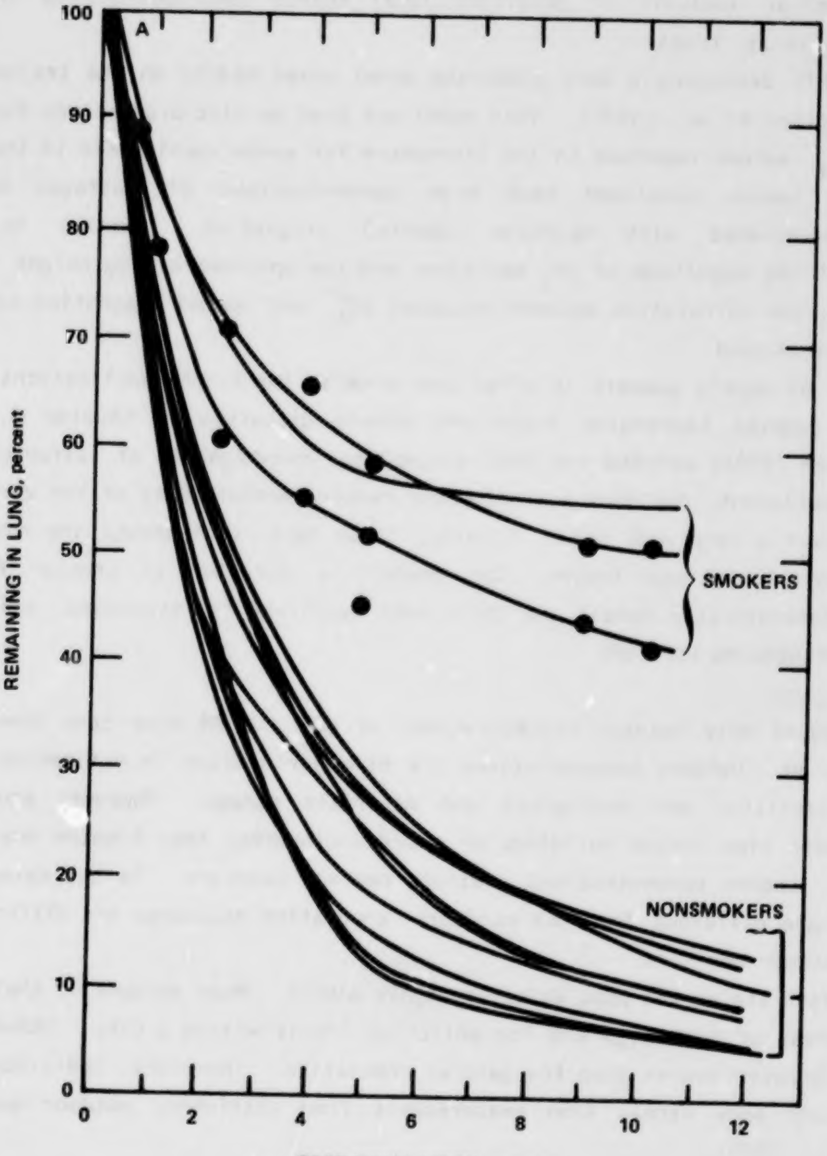


Figure 5-50. Retention of Au^{198} labeled Fe_2O_3 particles from human lungs; comparison of 9 non-smoking subjects with three smoker subjects.

Source: Cohen et al. (1979).

whom were smokers. Ten months following exposures to a known quantity of metallic dust, the nonsmokers had cleared 85 to 95 percent of the dust from their lungs. At the same time, smokers had retained about half of their original dose Unfortunately, there are few other studies that help in understanding these individual variations.

In this section the two major factors influencing human exposure to SO_2 and PM, indoor exposures and activity variations, are presented because they are important in understanding health effects. First the systematic differences between indoor and outdoor concentrations of SO_2 and fine and coarse particles are discussed. Then the limited evidence is presented for varying exposures of individuals depending on their activities.

5.8.2 Indoor Concentrations of Sulfur Dioxide

Indoor concentrations of SO_2 are invariably lower than outdoors, usually by a factor of two (Spengler et al., 1979). Since indoor sources of SO_2 (such as matches, natural gas odorants) are usually negligible, virtually all SO_2 indoors originated outdoors. Lower indoor concentrations are commonly attributed to SO_2 removal by contact with wall coatings, furniture, flooring and carpets, air conditioning filters, and the like.

Removal of SO_2 inside chambers and rooms has been shown to be a function of the material present and the relative humidity (RH). Cox and Penkett (1972) measured the decay rate of SO_2 inside containers. Reaction rates were found to be first order in SO_2, and irreversible absorption occurred on the walls. The removal rates were very sensitive to the RH. As relative humidity increased, so did SO_2 removal, approaching a maximum value at slightly above 80 percent RH (Cox and Penkett, 1972). Spedding studied SO_2 sorption by indoor surfaces (Spedding and Rowlands, 1970; Spedding, 1970; Spedding et al., 1971). The surface finish on wallpaper affected sorption rates of SO_2. Conventional wallpaper showed better uptake than polyvinyl chloride (PVC) wallpaper. Hard woods sorbed SO_2 better and to a greater depth than did softer woods. Sulfur dioxide sorption was also measured for leather surfaces. The rate of absorption seemed to be influenced by the tanning process and the dyes used.

Walsh et al. (1977) measured sorption of SO_2 by typical indoor surfaces including wool carpets, wallpaper, and paint. Absorption rates, as measured by deposition velocities, were lower for carpets with an acidic pH than those which were either neutral or alkaline. Sorption of SO_2 appeared to be irreversible. When carpets were preexposed to an SO_2 concentration equivalent to 27 years of exposure at 30 $\mu g/m^3$, the amount of SO_2 uptake was reduced by a factor of three. Fresh emulsion paints had the highest deposition velocity or SO_2 absorption rates, and vinyl wallpaper had the lowest. It was concluded that the most effective sorbing materials likely to be present inside homes are cellulose wallpaper, furniture fabrics, and wool carpets. Therefore, most studies report lower levels of SO_2 indoors than outdoors.

Anderson (1972) reports that indoor SO_2 concentrations averaged 51 percent of the outdoor concentrations over a 7.5-month period of paired 24-hour sampling inside and outside a single room. The correlation coefficient was only 0.52 (Anderson, 1972). Biersteker et al. (1965)

analyzed over 800 paired samples from the living rooms and exteriors of 60 Rotterdam homes. Indoor SO_2 levels averaged 20 percent of the outdoor levels and were lower for newer homes than for older homes. This may imply longer air turnover times in the newer homes and/or a "fresher" surface area for SO_2 absorption (Biersteker et al., 1965). Weatherly (1966) measured SO_2 and smoke levels inside and outside a building in central London in early 1960. Indoor SO_2 levels were always lower than the corresponding ambient conditions, averaging 40 percent. Spengler et al. (1979) reported on paired SO_2 monitoring inside and outside at least 10 homes in each of 6 cities. Figure 5-51 displays the annual SO_2 concentration in $\mu g/m^3$ averaged across each community's indoor/outdoor network of monitors (May 1977 to April 1978). The cities were: Portage, WI; Topeka, KS; Kingston and Harriman, TN; Watertown, MA; St. Louis, MO; and Steubenville, OH. Where ambient levels were high, the indoor concentrations were 30 to 50 percent of the ambient levels. In Kingston, many of the indoor levels were less than the minimal detectable level and were averaged in as zeros. This was not done for Portage and Topeka, where ambient levels were very low; hence the indoor SO_2 levels in these cities appear to be reduced by only 20 percent of the outdoor concentrations.

The seasonal indoor/outdoor pattern for each city depends on the SO_2 sources in each city and the use of air conditioning. These differences can be seen by comparing the monthly mean indoor and outdoor SO_2 concentrations for Watertown and Steubenville, as shown in Figures 5-52 and 5-53. In Watertown, SO_2 was primarily derived from sulfur-laden fuels. The ambient levels rose in the winter as more residual and distillate oil was used for space heating. The indoor/ outdoor ratios became small because homes were sealed more tightly. In the summer, ambient levels decreased, but the indoor/outdoor ratio approached unity because of increased ventilation. In Steubenville, the summer SO_2 levels were not substantially reduced from winter values, since residential and commercial space heating was not the primary source of SO_2 in this area. Yet the reduced indoor levels continued since more air conditioning was used in Steubenville (50 percent of homes sampled). Even in homes without air conditioning, summer levels were reduced by 30 to 40 percent.

While most information supports the idea of lower indoor SO_2 concentrations, exceptions are known. Yocom et al. (1971) found one home, heated by a leaky coal furnace, in which the indoor SO_2 level was periodically 10 times the outdoor level. Bierstecker et al. (1965) also found leaking flue gas contributions indoors.

However, the principal body of evidence suggests that indoor exposures are generally about half that found outdoors. Consequently, highest exposure levels are likely to be incurred by people who spend time outdoors near local SO_2 sources.

5.8.3 Particle Exposures Indoors

5.8.3.1 Introduction--Available data on indoor particle levels were collected by a wide variety of measurement procedures ranging from dustfall to condensation nuclei counting Earlier in this chapter and in Chapter 3, it was noted that the various particle measurement

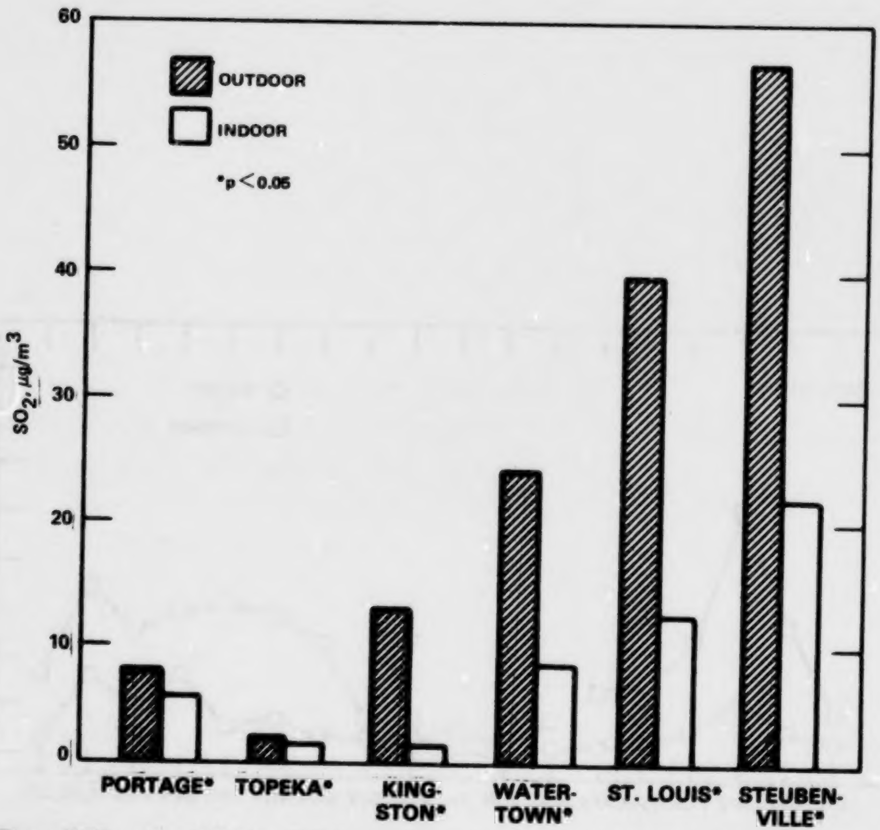


Figure 5-51. Annual sulfur dioxide concentrations averaged across each community's indoor and outdoor network (May 1977 – April 1978).

Source: Spengler et al., 1979.

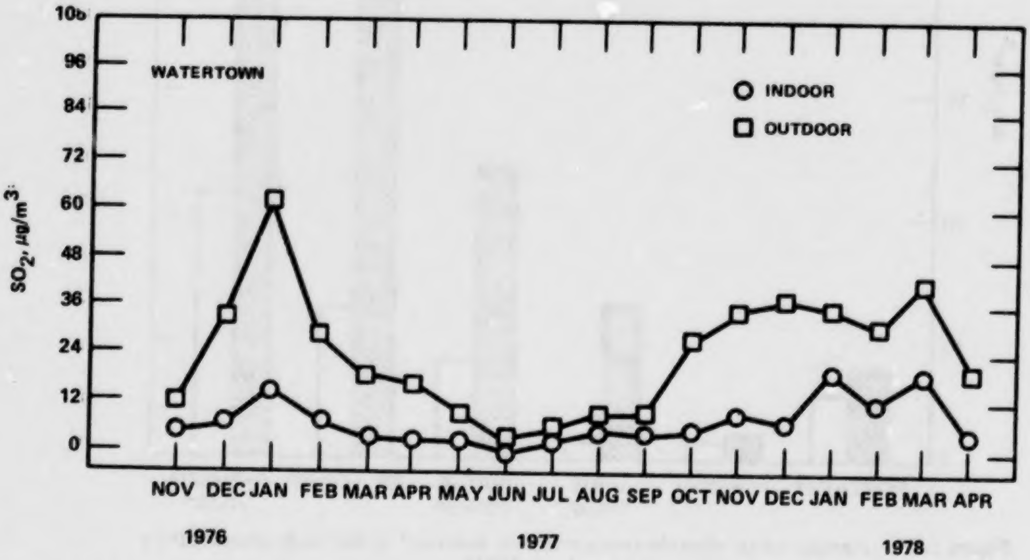


Figure 5-52. Monthly mean SO_2 concentrations averaged across Watertown's indoor and outdoor network (November 1976 – April 1978).

Source: Spengler et al. (1980).

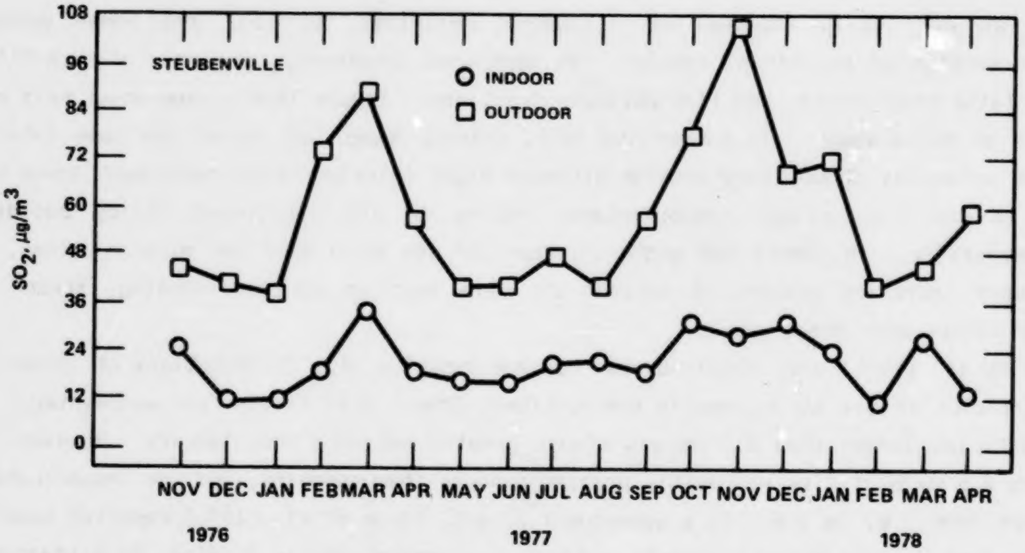


Figure 5-53. Monthly mean SO_2 concentrations averaged across Steubenville's indoor and outdoor network (November 1976 – April 1978).

Source: Spengler (1980).

procedures have definite particle size biases. For example, dustfall and TSP mass measurements are dominated by coarse particles, while light scattering and nuclei counting, on the one hand, and smokeshade and coefficient of haze on the other, are better measures of fine particles and particulate carbon mass (one fine particle component), respectively.

Evidence from these techniques has produced a consistent view of indoor and outdoor particle concentrations and sources, and this view is presented below by separate consideration of coarse- and fine-particle studies. Table 5-23 summarizes available studies by particle measurement technique.

5.8.3.2 Coarse-Particle Concentrations Indoors--Particles larger than 5 or 10 μm tend to settle from the air, and two studies using dustfall collection techniques suggest that these particles are greatly reduced indoors. Whitby et al. (1957) studied dustfall in offices, laboratories, and homes. Average indoor dustfall was only 15 to 20 percent of the outdoor level. No significant differences were found among residential or business locations. Schaefer et al. (1972) found indoor dustfall about one-eighth outdoor values in a study of 30 residential sites in four cities. There was little correlation between indoor and outdoor levels. Dustfall was higher in homes where windows were open.

Yocom et al. (1971) studied TSP in public buildings, offices, and homes using a scaled-down version of the hi-vol sampler. As mentioned previously, the mass of such filter samples contains both coarse- and fine-particle fractions. Indoor levels were about half outdoor levels on the average. In summer and fall, private homes had almost the same interior daytime TSP values as those found outside although night interior levels were much lower than outside. In the same study, indoor/outdoor ratios in air-conditioned office buildings differed seasonally. In summer and winter, indoor TSP was about half the outdoor values, but in fall, when increased volumes of outdoor air were used in air conditioning, indoor and outdoor TSP values were about equal.

Yocom et al. (1970) also obtained some cascade impactor size distributions of indoor and outdoor particles in six structures in the Hartford, Conn., area in the fall and winter. The mass of particles larger than 2.5 μm was always greater outdoors than indoors. However, the mass of sub-2.5 μm particles was mostly greater indoors than outdoors, and the indoor/outdoor ratio varied from 0.63 to 2.6. In a subsequent report, Yocom et al. (1971) reported substantially increased organic particle levels indoors, confirming similar findings by Goldwater et al. (1961). This result was attributed to smoking and cooking, indoor activities that could also increase fine-particle mass.

Alzona et al. (1979) reported elemental analyses for calcium and iron, normally coarse-particle components, and for zinc, lead, and bromine, components of fine particles. In these studies, an experimental room was cleared of airborne PM and then allowed to come to equilibrium under controlled penetration of outdoor ambient air. Experiments were carried out with windows "cracked" open and wide open and with windows and/or room surfaces covered with plastic sheets. Filter samples drawn throughout the experiment were analyzed by X-ray

TABLE 5-23. SUMMARY OF INDOOR/OUTDOOR (I/O) PM MONITORING STUDIES BY METHOD

Method	Author	Location	Building type	Number of sites	Month or season	Sampling period	Mean		Number of samples	I/O ratio
							Indoor	Outdoor		
Dustfall[a]	Whitby et al. (1957)	Minneapolis	Residential	12	Annual	--	0.54	2.86	--	0.19
			Lab & office	30	Annual	--	0.47	2.86	--	0.16
	Schaefer et al. (1972)	Chicago, Washington, Atlanta, Austin-San Antonio	Residential		Mar.-Aug.	--	0.44	3.48	26	0.12
Total suspended PM[b]	Yocom et al. (1971)	Hartford, CT	Public	2	Summer	12 hr	59	111	--	0.53
					Fall	12 hr	58	119	--	0.49
					Winter	12 hr	63	277	--	0.23
			Office	2	Summer	12 hr	53	108	--	0.49
					Fall	12 hr	31	50	--	0.60
					Winter	12 hr	42	122	--	0.35
			Residential	2	Summer	12 hr	62	67	--	0.94
					Fall	12 hr	53	77	--	0.69
					Winter	12 hr	43	97	--	0.44
Smoke[b]	Whitby et al. (1957)	Minneapolis	Lab & office	--	--	--	42	74	--	0.57
			Residential	--	--	--	46	74	--	0.62
		Louisville	Lab & office	--	--	--	101	124	--	0.81
			Residential	--	--	--	121	124	--	0.98
	Goldwater et al. (1961)	New York	Lab & office	12	Feb.-Mar.	--	149	263	12	0.57
			Residential	18	Feb.-Mar.	--	164	179	18	0.91

TABLE 5-23 (continued)

Method	Author	Location	Building type	Number of sites	Month or season	Sampling period	Mean Indoor	Mean Outdoor	Number of samples	I/O ratio
	Jacobs et al. (1962)	New York	Residential	17 --	Apr.-May	--	239	226	17	1.06
	Weatherly (1966)	London	Office	1	Jan.-Mar.	1 hr	195	205		0.95
	Biersteker et al. (1965)	Rotterdam	Residential	60	Winter	24 hr	153	184	800	0.84
	Berdyev et al. (1967)	Dushambee	Residential 1st floor	1	Summer	--	1270	960	8	1.32
		U.S.S.R.	Residential 2nd floor	1	Summer	--	660	960	9	0.60
	Anderson (1972)	Arhus, Denmark	Classroom	1	Sept.-Apr.	24 hr	27	34	150	0.81
Respirable particless[b]	Binder et al. (1976)	Ansonia, CT	Smoking homes	11	Sept.-Dec.	24 hr	132	58	11	2.28
			Non-smoking homes	9	Sept.-Dec.	24 hr	93	58	9	1.60
Particle counts[c]	Parvis (1952)	Italy	Residential	5	--	--	45.7	97.6	--	0.47 CN
					--	--	1000	1036	--	0.97 PC
	Ishido et al. (1956)	Osaka	Apartment	1	March	24 hr	1287	1528	--	0.84
					May	24 hr	978	1047	--	0.91
					June	24 hr	738	752	--	0.98
					Nov.	24 hr	--	1897	--	--

TABLE 5-23 (continued)

Method	Author	Location	Building type	Number of sites	Month or season	Sampling period	Mean		Number of samples	I/O ratio
							Indoor	Outdoor		
	Ishido (1959)	Osaka	Apartment	1	--	--	706	619	--	1.14
			Residential	1	--	--	662	678	--	0.98
			Hospital	1	--	--	1611	1595	--	1.01
			School	1	--	--	2382	2346	--	1.02
	Jacobs et al. (1962)	New York	Office & lab	12	--	--	424	481	--	0.88
			Homes	18	--	--	705	472	--	1.49
	Megaw (1962)	England	Test building	1	--	--	--	--	5	0.66
	Lefcoe and Inculet (1975)		Homes (AC & ESP)	2	Annual	--	510^d	227^d	--	1.46
						--	156^e	59^e	--	2.60
Coefficient of haze^g	Whitby et al. (1957)	Minneapolis	Residential	--	--	--	0.6	1.05	--	0.57
			Lab & office	--	--	--	1.0	1.05	--	0.95
		Louisville	Residential	--	--	--	2.4	2.6	--	0.92
			Lab & office	--	--	--	2.8	2.6	--	1.06
	Carey et al. (1958)	Cincinnati	Residential	--	Oct.-Dec.	--	2.1	3.8	--	0.55
	Shephard (1959)	Cincinnati	Residential	9	Jan.	--	2.2	2.7	--	0.86
				9	Feb.	--	2.0	2.3	--	0.89
				9	Mar.	--	1.6	1.8	--	0.85
				9	Apr.	--	1.6	1.7	--	0.94
				--	May	--	--	1.0	--	--
				--	June	--	0.8	0.9	--	0.88
				--	July	--	0.8	0.8	--	1.00
				--	Aug.	--	1.3	0.8	--	1.63
				9	Sept.	--	0.8	0.5	--	0.80
				9	Oct.	--	1.5	0.9	--	1.15
				9	Nov.	--	1.7	1.1	--	0.89
				9	Dec.	--	1.8	1.5	--	1.06

TABLE 5-23 (continued)

Method	Author	Location	Building type	Number of sites	Month or season	Sampling period	Mean Indoor	Mean Outdoor	Number of samples	I/O ratio
	Yocom et al. (1971)	Hartford, CT	Public	2	Summer	--	0.32	0.36	--	0.90
					Fall	--	0.33	0.34	--	0.97
					Winter	--	0.36	0.51	--	0.69
			Office	2	Summer	--	0.29	0.41	--	0.70
					Fall	--	0.20	0.26	--	0.78
					Winter	--	0.37	0.54	--	0.88
			Homes	2	Summer	--	0.41	0.42	--	0.98
					Fall	--	0.28	0.30	--	0.93
					Winter	--	0.32	0.39	--	0.82
Piezoelectric microbalance	Repace and Lowrey (1980)	Metropolitan Washington, DC	Public (no smoking)	3	March-June	20 min.	29 to 55^f	40 to 55^f	3	0.66 to 1.38
			Public (smoking)	13	March-June	2 min (I) 5 min (O)	86 to 697^f	22 to 63^f	4-25 (I) 13 (O)	1.56 to 11.62

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[a] Measured as g/m^2/month.
[b] Measured as μg/m^3.
[c] Measured as number/cm^3.
[d] Particles >0.3 μm.
[e] Particles >0.5 μm.
[f] Particles >1.0 μm.
[g] Measured as COH/1000 linear ft.

Note: 1 ppm SO_2 = 2620 ug/m^3.
1 ppm NO_2 = 1885 ug/m^3.

excitation for elements of known outdoor origin (Fe, Zn, Pb, Br, Ca). Within several hours, equilibrium was reached in which the indoor/outdoor ratio was typically 0.3 (see Tables 5-24 and 5-25). On the basis of the indoor/outdoor element ratios, they conclude that remaining indoors with doors and windows partially closed reduces outdoor dust exposure by two-thirds. The indoor/outdoor ratios for the coarse-particle components, calcium and iron, were lower than for the fine-particle components zinc, lead and bromine. Therefore, it appears that tracer components of coarse particles do not penetrate any of these structures as readily as the fine components.

5.8.3.3 Fine Particles Indoors--In addition to the cascade impactor studies mentioned earlier in conjunction with the coarse-particle discussion, there have been several recent reports of sub-3.5 μm particle mass measurements indoors and outdoors.

Repace and Lowrey (1980) reported even larger indoor/outdoor contrasts, which they attribute to smokers. Using a piezoelectric microbalance, they sampled fine particles (0.01 to 3 μm) inside and outside a variety of public places, many of them restaurants. In the absence of smokers, the indoor/outdoor ratios were in the range of 1:1, comparable with ratios reported by investigators using other methods. With smokers present, indoor/outdoor ratios ranged to over 11:1 (Table 5-23).

Binder et al. (1976) used hi-vol air samplers outdoors and personal samplers equipped with a 3.5 μm cutoff device. The personal monitors were carried by school children who spent 60 to 80 percent of their time indoors. In homes where there were smokers, the indoor fine-particle mass was almost twice the outdoor TSP.

Spengler and Dockery have measured indoor and outdoor levels of sub-3.5 μm particulate mass using cyclone-equipped membrane filter samplers in the same six cities noted in Section 5.8.2 (Spengler et al., 1981; Dockery and Spengler, 1981; and Dockery, 1979). Figure 5-54 presents annual average values for all sites in the six cities. In all cities except Steubenville, Ohio, the indoor fine-particle level was higher than outdoors. Steubenville, an industrialized community, also had the highest annual average outdoor level. Table 5-26 presents arithmetic averages for all homes in this study stratified by numbers of smokers in the household (Dockery, 1979). It is apparent that in the absence of smoking, indoor and outdoor levels of fine-particle mass are almost the same. However, smoking contributes very significantly to indoor levels. Dockery (1979) calculated that a one pack/day-smoker contributes about 18 $\mu g/m^3$ to inside fine-particle mass, and this level is increased by the use of air conditioning, presumably because of recirculation, to 43 $\mu g/m^3$.

TABLE 5-24. MEASUREMENTS IN PRINCIPAL ROOM OF STUDY[a]

Case	Number of runs	Conditions	I/O				
			Ca	Fe	Zn	Pb	Br
J	3	Normal	0.10	0.17	0.52	0.49	0.33
K	2	Plastic over windows	0.10	0.15	0.71	0.17	0.17
L	1	Window wide open	0.52	0.81	0.93	1.2	1.0
M	2	Window cracked open	0.20	0.16	0.69	0.55	0.53
N	6	All surfaces plastic covered	0.02	0.12	0.24	0.15	0.20
P	3	All but windows plastic covered	0.10	0.15	0.58	0.57	0.32

Source: Alzona et al. (1979).

[a] The study room in all these cases was the same 12 m^2, old university building room listed below in Table 5-25 as case J.

TABLE 5-25. MEASUREMENTS IN VARIOUS CLOSED ROOMS

Case	Number of runs	Type of room	Number of windows	I/O				
				Ca	Fe	Zn	Pb	Br
A	1	10 m^2, new univ. bldg.	0	--	<0.1	--	<0.1	<0.1
B	1	50 m^2, old univ. bldg.	2	--	0.33	--	0.25	0.43
C	1	30 m^2, bedroom, tight home	8	--	0.27	--	0.70	0.58
D	1	20 m^2, attic, tight home	2	--	0.10	0.36	0.40	0.29
E	1	20 m^2, bedroom, leaky home	2	0.05	0.33	--	0.47	0.22
F	1	Chevrolet Vega	6	--	0.27	--	0.41	0.36
G	1	Datsun 440	6	--	0.09	0.21	0.12	0.24
H	2	20 m^2, old chem. lab	(3)	0.08	0.13	0.37	0.31	0.25
I	2	20 m^2, new univ. bldg.	3	0.15	0.54	0.55	0.47	0.58
J	3	12 m^2, old univ. bldg.	(3)	0.10	0.17	0.52	0.49	0.33
Average (except A)				0.10	0.24	0.41	0.42	0.36

Source: Alzona et al. (1979).

TABLE 5-26. RESPIRABLE PARTICULATE CONCENTRATIONS OUTDOORS AND INDOORS BY AMOUNT OF SMOKING[a]

Location	Number of homes	Number of samples	Mean concentration, $\mu g/m^3$	Standard deviation of home means
Outdoor	74	2598	22.3	12.7
Indoor, no smokers	38	1328	24.0	11.4
Indoor, 1 smoker	22	712	42.8	22.2
Indoor, 2+ smokers	9	323	74.5	37.9

[a] Data averaged across network of samples in six communities for 1977.
Source: Dockery (1979).

Spengler et al. (1981) also reported that indoor SO_4^{2-} (a fine-particle component) levels were significantly lower than outdoor levels, but that gas cooking stoves can increase levels by about 1 $\mu g/m^3$ (Dockery and Spengler, 1981). Yocom et al. (1971) found that lead indoor/outdoor ratios were greater than TSP ratios. Taken with the previously mentioned Alzona et al. (1979) study, it appears that most fine particle components analyzed are found in high proportion indoors.

A number of studies have reported indoor measurements of smokeshade or COH, both estimates of fine-particle carbon. Whitby et al. (1957), Shephard et al. (1958), and Weatherly (1966) all found smokeshade values inside and outside buildings to be nearly equal. Goldwater et al. (1961) found indoor smoke about 75 percent of the outside levels in 30 New York sites, but that difference was not significant. Jacobs (1962) found no indoor/outdoor differences in a followup New York study. Anderson (1972) found nearly equal and highly correlated smoke values in a classroom and outdoors in Denmark. Biersteker et al. (1965), on the other hand, found no correlation between indoor and outdoor smoke in a winter study of 60 homes in Rotterdam. Whitby et al. (1957) and Yocom et al. (1971) both reported that indoor COH values were much closer to outdoors than either dustfall or TSP. Apparently, the fine carbon particles measured by these techniques effectively penetrate buildings.

A similar conclusion is reached in indoor/outdoor light-scattering studies. Since scattering of visible light is caused by the range of particles from about 0.2 to 1.0 μm, measurements using this technique provide another index of fine-particle mass. Indoor and outdoor light-scattering values were found to be the same and highly correlated in Japan (Ishido, 1959; Ishido et al., 1956), in Italy (Parvis, 1952; Romagnol, 1961), and in New York (Jacobs et al., 1962).

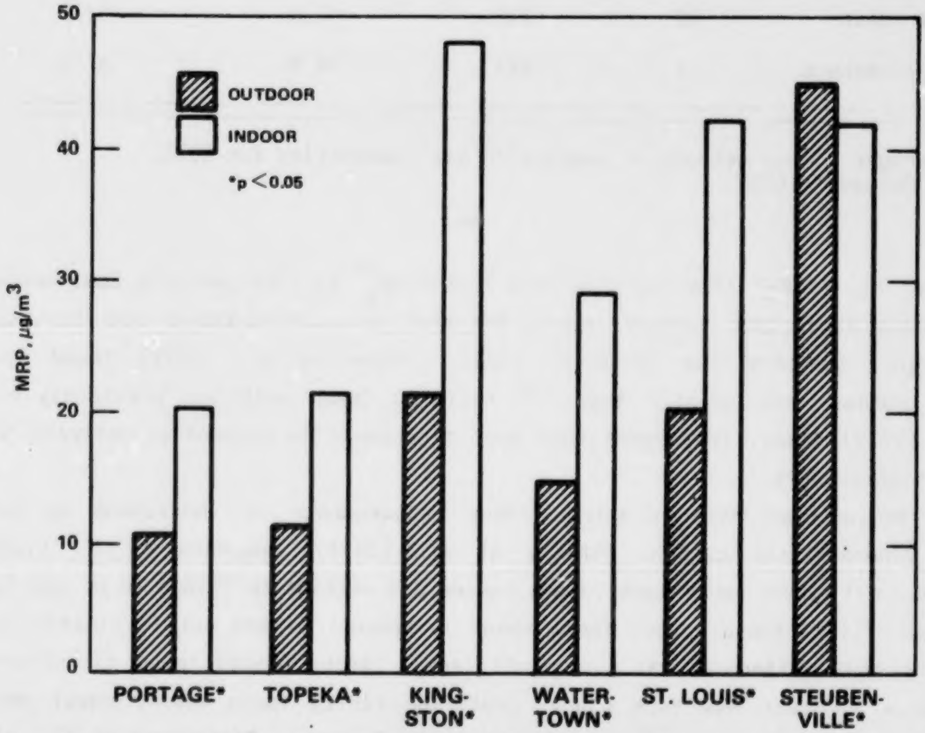


Figure 5-54. Annual respirable particulate concentrations averaged across each community's indoor and outdoor network (May 1977 – April 1978).

Source: Spengler et al. (1980).

Therefore, fine particles readily penetrate buildings and occur inside to about the same extent as outdoors. Indoor activity adds incrementally to outdoor levels and, frequently, somewhat higher levels of fine particles are observed indoors. Smoking adds very materially to indoor levels.

5.8.4 Monitoring and Estimation of Personal Exposures

In previous sections of this chapter, the spatial and temporal variations in the concentrations of SO_2 and of fine and coarse particles and their components were summarized for both outdoor and indoor exposures. However, looking forward to health effects summarized in Chapters 11 to 14, there is still one element of exposure remaining for discussion. In addition to the particle concentrations measured by long integrating-time monitors (i.e., long-term doses of pollutants), people are exposed to short-term high concentrations. Unfortunately, sufficient data do not exist to establish the relative importance of concentration and time of exposure. There is, however, evidence (cited in Chapter 12) for gaseous SO_2 and particles that long-term exposures can cause adverse health effects. There is also evidence that a short burst of pollutant exposure can cause adverse health effects. Therefore, these peaks in exposure are likely to be important, and there is some evidence that peaks occur both indoors and outdoors. For example, earlier in this chapter it was noted that high levels of SO_2 occur periodically close to intense sources. Obviously, people passing through such an area, even though they are not resident there, receive a high short-term dose. On roadways, particle concentrations tend to be very high because of resuspension of road dust. Clearly, travelers experience such concentrations at least for the time they are in traffic. As pointed out earlier in this section, an individual's daily activities, the places visited, and activities in the home all play a role in that person's exposure.

For example, Repace et al. (1980) followed an individual's daily exposure with a portable particle monitor and correlated these measurements with activities. Figure 5-55 shows time series plots of PM concentrations to which James Repace, the principal investigator, was exposed on October 16, 1979. Sharp peaks were evident in traffic, indoor smoking areas, and his own home, particularly in the kitchen. Obviously, controlling outdoor air pollutant levels would have little influence on his exposure to short-term doses of particles except for those incurred on roadways. There have been other recent reports of statistical studies of the relationships among personal, indoor, and outdoor particle concentrations.

In a personal monitoring study designed to test the relationships between outdoor concentrations and personal exposures and to estimate activity concentrations, Spengler et al. (1980) collected 12-hour respirable particle samples for 15 days on 45 individuals in Topeka, Kans. Particle concentrations experienced by monitored individuals were 2.5 times greater than average outdoor levels for this time interval. Further, there was no correlation between the outdoor level and the personal exposure of individuals. Variation in outdoor concentrations.

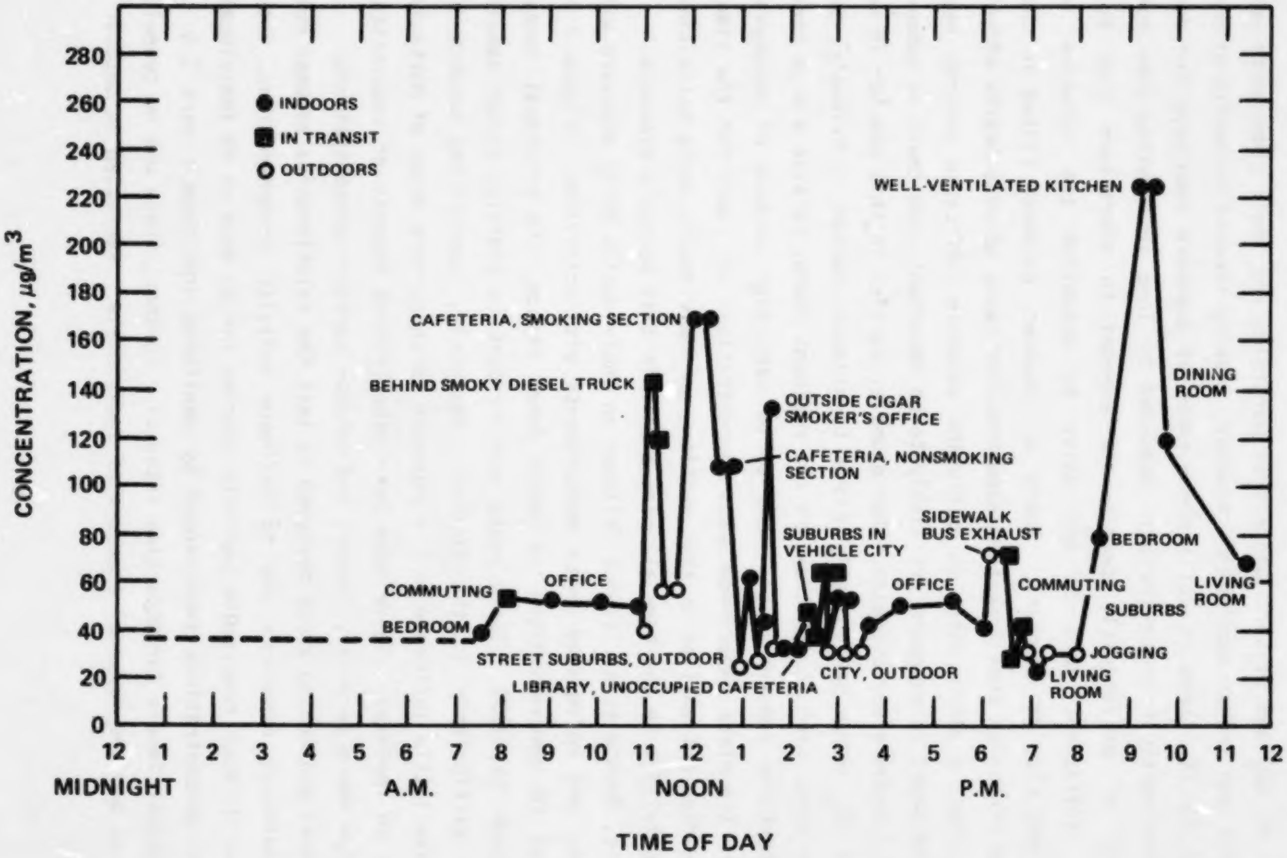


Figure 5-55. An example of personal exposure to respirable particles.

Source: Repace et al. (1980).

explained only 4 percent of the variability in personal concentrations experienced. On the other hand, indoor respirable particle levels explained a fair amount of the variability in personal exposure; for men, indoor levels accounted for 25 percent of their exposure variation while for women 50 percent was explained by this variation. It appears that somewhere in the daily activities of these individuals, their exposure was substantially greater than that measured by outdoor monitors and, further, the variation in exposure is not measured adequately by fixed indoor monitors either. Passive smoke exposure accounted for a significant portion of the increment above outdoor levels. Figure 5-56 plots the histograms of concentrations for both volunteers who reported no passive smoke exposure during the day and those who reported some exposure to passive smoke. The means were 20 $\mu g/m^3$ for nonsmoke-exposed samples versus 40 $\mu g/m^3$ for smoke-exposed samples.

In Figure 5-57, the daily mean concentrations for all outdoor, indoor, and personal samples are presented. There is the suggestion that the variation in outdoor concentrations causes variations in indoor and personal concentrations. However, variations in indoor concentration cause considerable variance in individual exposures.

As an alternative to direct measurement (monitoring), typical personal exposures may be estimated on the basis of information on indoor and outdoor concentrations and human activity patterns.

The exposure to particles and gases that one experiences will be ultimately determined by location and activity. Certainly, locational and activity patterns are very complex in our society. They are functions of age, sex, social, economic, and educational factors. While a limited data base exists on activity patterns within our population and on the distribution of smokers, housing stock, and various other building factors, an exhaustive discussion is not appropriate for this document.

Time budget studies of the U.S. population indicate that on the average, 90 percent of an individual's time is spent indoors. Between 5 and 10 percent of the time is spent in transit in a vehicle. Considering these figures, the indoor environment is very important in determining the time-weighted average exposure.

However, the time-weighted average is only one measure of pollution exposure. Time spent outdoors is variable. The time outdoors varies by the time of day and year, among regions of the country and among different categories of people. Therefore, in regard to the concern for indoor pollution, the fact that short-term peak ambient concentrations may be an important component of exposure should be remembered.

Much work remains to be done on personal exposures to gases and particles. Based on current understanding, the following qualitative statements can be made:

1. Depending on spatial gradients in ambient air, personal exposures to SO_2 should be less than the outdoor concentrations.

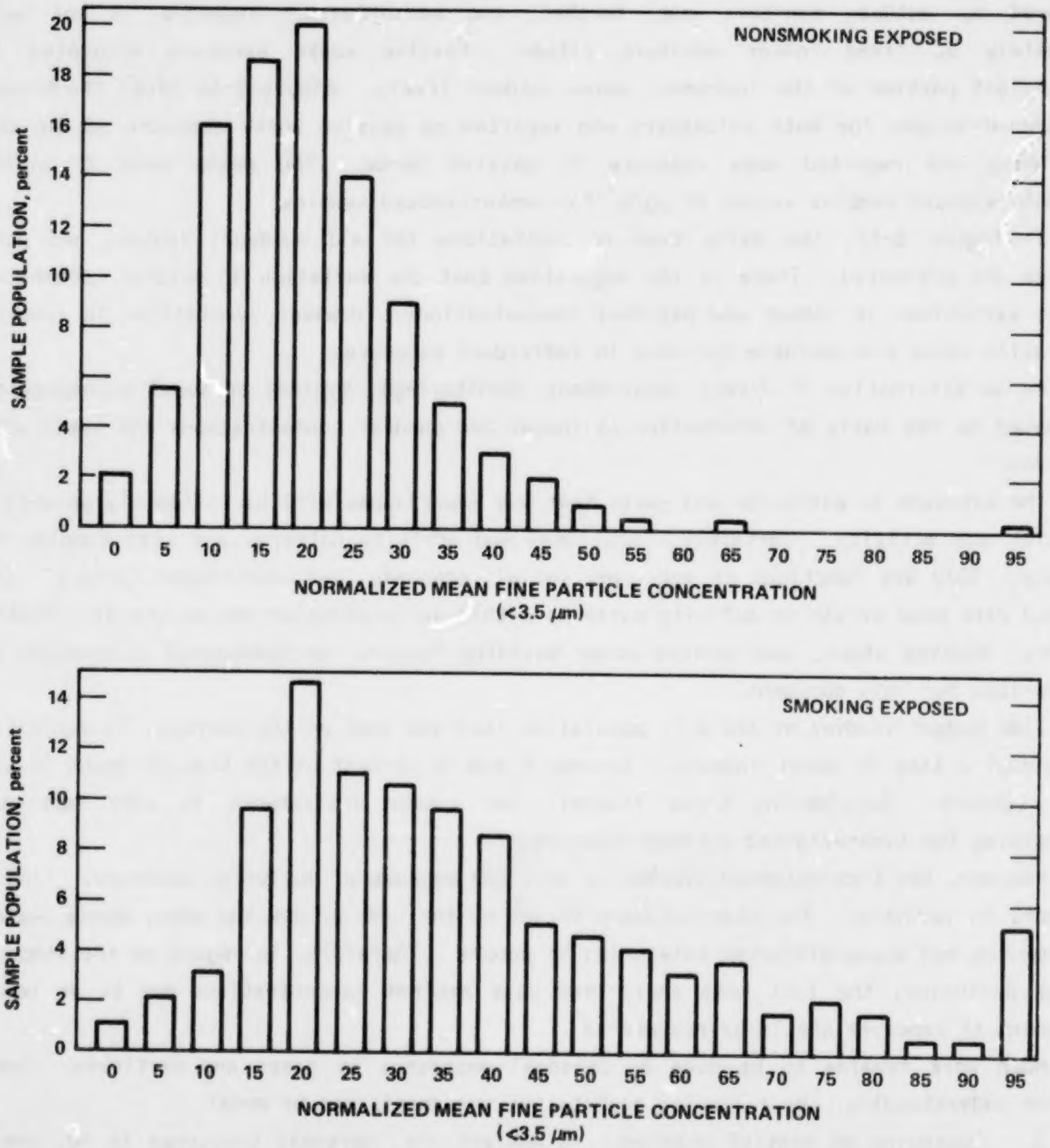
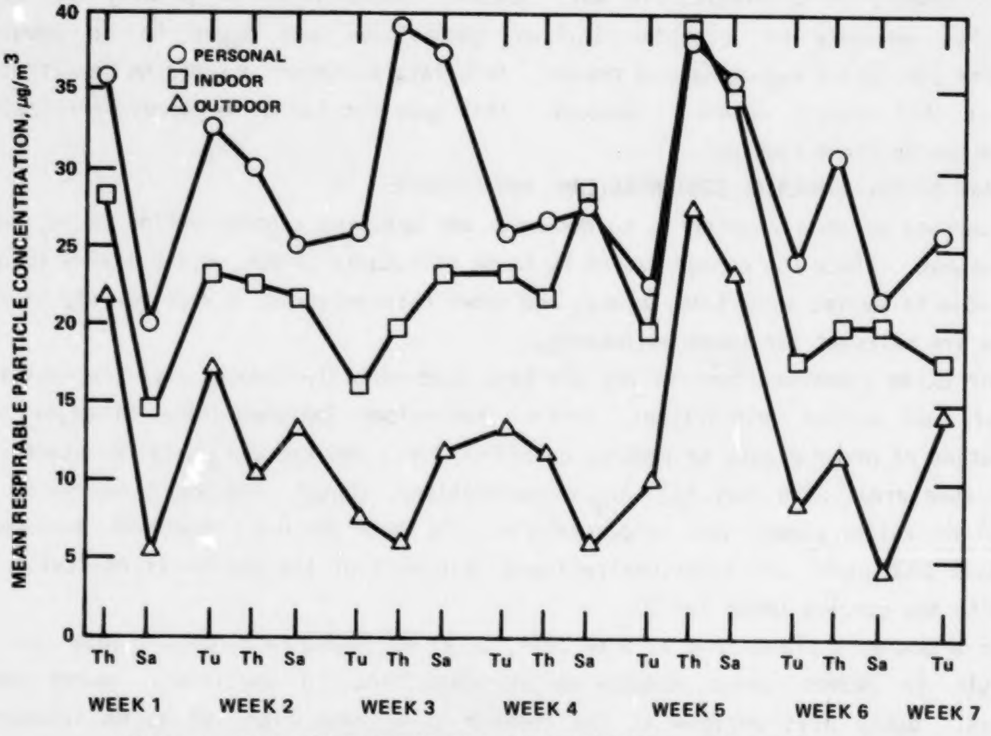


Figure 5-56. Normalized distribution of personal (12-hour) exposure samples ($\mu g/m^3$) for non-smoke exposed and smoke exposed samples.

Source: Spengler and Tosteson (1981).



DAILY AVERAGE CONCENTRATIONS FOR THE ENTIRE GROUP OF 46 SUBJECTS IN THE TOPEKA STUDY

Figure 5-57. Daily mean indoor/outdoor and personal concentrations ($\mu g/m^3$) of respirable particles. Daily means averaged over 24 homes and outdoor locations and up to 46 personal samples. Samples collected during May and June 1979.

Source: Spengler et al. (1980).

2. Depending on activity times and building characteristics, longer term exposure could be less than half the ambient concentrations.

3. For estimates of personal exposure to particle mass concentration, the ambient measurement appears to be a poor predictor. While ambient concentrations exert an effect, personal activities and indoor concentrations cause personal exposures to vary substantially.

4. Tobacco smoke is an important contributor to indoor and personal exposures.

5. Personal exposures to the components of suspended PM of outdoor origin and contained in the micrometer and submicrometer size fraction may be estimated by ambient measurements. The smaller size particles of toxic trace elements (V, Cd, Ni, Br, Se, etc.) and some organic and inorganic compounds (SO_4^{2-}, NO_3^-), which are exclusively of outdoor origin, penetrate the indoor environment in a predictable way. Outdoor measurements of primary and secondary fine-fraction aerosols in nonindustrialized communities may prove to be adequate to characterize population exposures and trends. This last statement assumes no important indoor sources for this typical outdoor component. This question certainly needs verification and quantification in field studies.

5.9 SUMMARY OF ENVIRONMENTAL CONCENTRATIONS AND EXPOSURE

The purpose of this chapter is to document the existing concentrations of SO_x and PM in the environment. Since the damage caused by these pollutants to man, other living things, and valuable objects varies with time, place, and other circumstances, a wide variety of exposure conditions are relevant for these pollutants.

Sulfur oxide concentrations in the air have been markedly reduced over the past 15 years because of fuel sulfur restrictions, control technology implementation on major sources, redistribution of power plants to regions outside cities, and the use of taller stacks. There are still some areas with very high SO_2 concentrations, though, and hourly values of 4000 to 6000 $\mu g/m^3$ are rather common near large smelters. In about 100 U.S. locations, maximum hourly values above 1000 $\mu g/m^3$ are occasionally found, but much of the nation is basically in compliance with the current NAAQS for SO_2.

After a downward trend from 1970 to 1974, total suspended PM concentrations have changed very little in recent years despite major reductions in stationary source emissions inventories. Dusty arid regions of the country still have high TSP as do industrialized cities in the East and Far West. Ninetieth-percentile values of 24-hour TSP (the values that are exceeded 10 percent of the time) are above 85 $\mu g/m^3$ in every part of the country except Alaska. Regional mean TSP values range from about 50 $\mu g/m^3$ in EPA Region I to 77 $\mu g/m^3$ in EPA Region IX.

Ambient airborne particles exist in two distinct size ranges, fine particles below about 1 μm, and coarse particles above about 3 μm. Rather little mass is in intermediate sizes. Except that both sizes are captured on filters, the two kinds have very little in common.

Fine and coarse particles differ in origin, chemical composition, geographical distribution and physical behavior.

Fine particles are composed mainly of (1) sulfate, nitrate, and ammonium ions, (2) organic substances from atmospheric photochemical conversions, and (3) carbon, organic matter, and metallic components directly emitted from combustion sources. Sulfate, most often in the form of neutral ammonium sulfate, but sometimes in association with acidity as NH_4HSO_4 or H_2SO_4, is the principal component, often accounting for 40 percent of fine-particle mass. Sulfate and NO_3 ions are present in high concentrations during both summer and winter episodes over very large sections of the eastern United States. This area experiences 10 μg/m^3 or greater SO_4^{2-} levels for one or two periods up to a month or more every year. The affected region is so large in scope that no real background levels of fine particles are available for measurement east of the Mississippi. Sulfate and fine-particle levels are nearly the same in cities and in rural areas. Southern California experiences high levels of sulfates and nitrates, particularly during photochemical incidents. In that area, high levels of fine organic aerosols are also found, often exceeding 100 μg/m^3.

Toxic organic particulate matter and metals are mainly emitted from combustion and industrial sources, and their concentrations are highest in cities. Trends in fine-particle components have been mostly downward because of control measures taken, such as lead reductions in gasoline.

Coarse particles in air are stirred up by the wind and by machinery. Since these particles settle fairly rapidly, they tend to be high close to sources. In most cases the coarse particles account for two-thirds of TSP in dry regions like Phoenix, Oklahoma City, El Paso, or Denver in the summer. The overwhelming cause of high TSP is local dust, but in industrialized cities there is evidence that contributions of soot, fly ash, and industrial fugitive emissions are also present.

Coarse particles are mainly composed of silica, calcium carbonate, clay minerals, and soot. Chemical constituents found in this fraction include the elements silicon, aluminum, potassium, calcium, and iron together with other alkaline earth and transition elements. Organic substances are also found in coarse particles, although their source is unknown.

Much of this coarse material is road dust suspended by traffic action, and street levels of resuspended dust can be very high. Traffic on unpaved roadways can generate huge amounts of dust, which deposits on vegetation and can be resuspended by wind action. Rain and snow cover can reduce these emissions, but one study suggests that salting of roadways can be a major source of winter TSP. Probably, associated sand is also important. Industrial fugitive emissions can be even greater local sources of coarse particles, particularly from unpaved access roads, construction activity, rock crushing, and cement manufacturing.

The problem of tracing existing levels of particles to sources is being solved in part by a number of calculational methods generally categorized as source apportionment or source-receptor models. The results from chemical element balance calculations or factor analysis are available now for several cities. Apportionments for these cities are presented as examples of results to be expected in the future by application of these powerful methods.

Although outdoor concentrations of pollutants can be measured at particular sites, our highly mobile population can be exposed to either higher or lower values than community monitors show. Indoor values of SO_2 tend to be lower than outdoor levels because walls, floors, and furniture absorb SO_2. Indoor particle levels can be high because of smoking, cleaning operations, or normal activities. Exposure of individuals to SO_x and PM can vary more than community monitors show.

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6. ATMOSPHERIC TRANSPORT, TRANSFORMATION, AND DEPOSITION

6.1 INTRODUCTION

The preceding chapters discussed the physical and chemical properties of sulfur oxides and PM (Chapter 2); methods of measuring them (Chapter 3); their sources and emissions (Chapter 4); and measurements of ambient levels in urban and rural environments (Chapter 5). These chapters also discussed information relevant to parts of this chapter; whenever possible, reference is made to resource material in previous chapters. Emissions, which can be viewed as a model input, are discussed only in the context of their relevancy to air quality simulation modeling in the final section.

This chapter reviews our knowledge of the physical and chemical processes that contribute to the transport and diffusion, transformation and deposition of PM and sulfur oxides in the atmosphere and discusses the theoretical approaches for integrating these processes with source emission contributions through the use of mathematical models. Such integrating approaches help improve understanding of the complex processes that operate in polluted atmospheres. These source-receptor relationships provide a credable scientific basis for determining the nature and extent of emission control required to meet specified ambient air quality levels.

The concentration of a pollutant species at a fixed point in time and space after it has been emitted from a source at another given point depends on four fundamental factors: (1) emission--the rate of pollutant emitted and the configuration of its source; (2) transformation--the chemical and physical reaction processes that convert one pollutant species to another; (3) transport and diffusion--the movement and dilution of a pollutant species through time and space as a result of various meteorological variables; and (4) deposition--the removal of pollutant species through their interaction with land and water surfaces (dry deposition) and through interaction with precipitation or cloud droplets (wet deposition).

Figure 6-1 schematically illustrates the principal process pathways of airborne pollutants. Ideally, each of these processes should be treated explicitly in any air quality simulation model, but generally this is not the case.

The modeling approaches discussed here include explicit treatments of the dynamic physical and chemical atmospheric processes that simulate relationships between pollutant emissions and ambient air quality. More implicit statistical-empirical approaches, which deduce source contribution through analysis of empirical information only, are not within the purview of this chapter. A brief discussion of source-apportionment techniques that have shown considerable promise in developing source-receptor relationships for particulate matter is presented in Section 5.7 of Chapter 5.

6.2 CHEMICAL TRANSFORMATION PROCESSES

Chapter 2 presents a detailed discussion of the chemistry of SO_2 and other gases that react to form PM in the atmosphere. Section 6.2.1 summarizes the results of the atmospheric

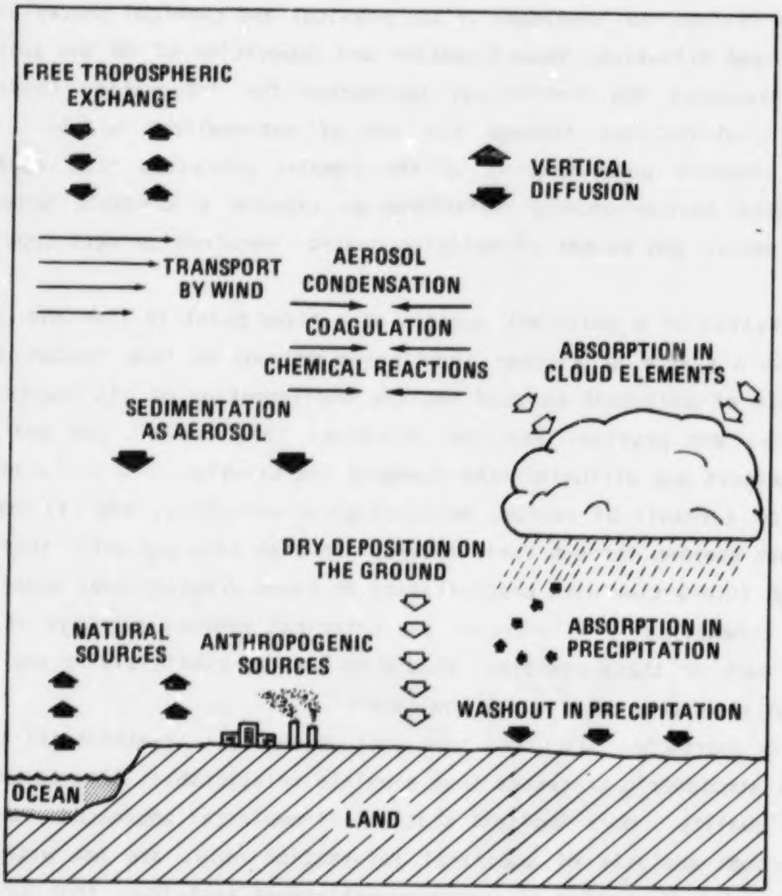
FREE TROPOSPHERIC EXCHANGE
VERTICAL DIFFUSION
TRANSPORT BY WIND
AEROSOL CONDENSATION
COAGULATION
CHEMICAL REACTIONS
ABSORPTION IN CLOUD ELEMENTS
SEDIMENTATION AS AEROSOL
DRY DEPOSITION ON THE GROUND
NATURAL SOURCES
ANTHROPOGENIC SOURCES
ABSORPTION IN PRECIPITATION
WASHOUT IN PRECIPITATION
OCEAN
LAND

Figure 6-1. Pathway processes of airborne pollutants.

Source: Adapted from Drake and Barrager(1979).

chemical transformation processes of SO_2 and PM presented in Chapter 2. Section 6.2.2 reviews the status of field measurements of the rate of SO_2 oxidation in industrial and urban plumes, and their contribution to elucidating the transformation pathway processes of SO_2 oxidation.

6.2.1 Chemical Transformation of Sulfur Dioxide and Particulate Matter

Present understanding of the homogeneous gas phase reactions of SO_2 indicates that the rate of SO_2 oxidation in the atmosphere is dominated by free radical reaction processes. The free radical species important to the SO_2 oxidation process are HO, HO_2, CH_3O_2, and other organic peroxyl species (RO_2, $R'O_2$, etc.). The concentrations of these radicals in the atmosphere depend on many factors, the more important of which are the concentrations of volatile organic compounds and nitrogen oxides (NO and NO_2) in the atmosphere, temperature and solar intensity. Theoretical estimates have shown that maximum SO_2 oxidation rates of 4.0 percent/h are possible in polluted atmospheres. Recent experimental rate constant determinations for the HO_2 and CH_3O_2 reactions with SO_2, however, indicate that these processes may not be as important as previously thought, and that the maximum,possible homogeneous SO_2 oxidation rate under optimum atmospheric conditions may only be of the order of 1.5 percent/h. This rate is a result of SO_2 reaction with HO radical only.

Present knowledge of heterogeneous pathways to SO_2 oxidation in the atmosphere indicates that the liquid phase catalyzed oxidation of SO_2 by Mn^{2+}, Fe^{3+}, and carbon are potentially important processes, as is oxidation by hydrogen peroxide. Theoretical estimates of atmospheric SO_2 oxidation rates by these processes are of the order of 10 percent/h. Unfortunately, the actual availability of these catalyzing substances in ambient fine PM is uncertain. The quantitative determination of rates of SO_2 oxidation by these processes has never been demonstrated under actual atmospheric conditions.

Processes that form organic and nitrate particles are thought to be dominated by homogeneous gas phase reactions. In the case of atmospheric nitrates, a significant production pathway is through reaction between HO free radical and NO_2, resulting in nitric acid ($HONO_2$) formation. The fate of nitric acid in the atmosphere is not well understood, though a portion of gaseous nitric acid is known to enter into an equilibrium with NH_3 to form particulate NH_4NO_3. Information on the production rates and mechanism details of organic particulate matter is limited. Available product information indicates that oxidation reactions involving the interaction of ozone, nitrogen oxides, and HO free radicals with higher molecular weight organics represent a major pathway to organic particle production.

6.2.2 Field Measurements on the Rate of Sulfur Dioxide Oxidation

The majority of atmospheric SO_2 oxidation studies have been carried out only in recent years, and most have involved power plant plumes. One reason for the late start in this research was the lack of adequate measurement technology for particulate sulfur, but recent developments (e.g., Huntzicker et al., 1978; Cobourn et al., 1978) seem to have alleviated this problem (see Chapter 3). Table 6-1 summarizes SO_2 oxidation rates, based on field measurements in power plant, smelter, and urban plume studies carried out from 1975 to 1980.

TABLE 6-1. FIELD MEASUREMENTS ON THE RATES OF SO_2 OXIDATION IN PLUMES[a]

Plume type/ location	SO_2 oxidation rate (percent/h)	Method	Reference
Power plants			
Keystone (Pennsylvania)	0-10	$^{32}S/^{34}S$ ratio, change with oxidation	Newman et al. (1975)
Labadie (Missouri)	0.41-4.9	Total change in particle volume	Cantrell and Whitby (1978)
Four Corners (New Mexico)	0.27-0.84	Submicron sulfate and SO_2 - change of ratio with time	Ursenbach et al. (1977)
Labadie and Portage des Sioux (Missouri) Muscle Shoals (Alabama) Kyger Creek (Ohio)	0-5	Particulate sulfur to total sulfur ratio	Forrest and Newman (1977)
Labadie (Missouri)	0-3	Particulate sulfur to total sulfur ratio	Gillani et al. (1978)
Four Corners (New Mexico)	2-8	CCN[b] production (CCN to SO_2 ratios)	Pueschel and Van Valin (1978)
Labadie (Missouri)	0-4	Particulate sulfur to total sulfur ratio	Husar et al. (1978)
Cumberland (Tennessee)	0-7	Particulate sulfur to total sulfur ratio	Meagher et al. (1978)
Great Canadian Oil Sands (Alberta, Canada)	0-3	Particulate sulfur to total sulfur ratio	Lusis et al. (1978)
Keystone (Pennsylvania)	0-5	Particulate sulfur to total sulfur ratio	Dittenhoefer and dePena (1978)
Centralia (Washington) Four Corners (New Mexico)	0-6	Total change in particle volume	Hobbs et al. (1979)
Four Corners (New Mexico)	0.15-0.5	CCN[b] production (CCN to SO_2 ratios)	Mamane and Pueschel (1980)

TABLE 6-1. (continued)

Plume type/ location	SO_2 oxidation rate (percent/h)	Method	Reference
Leland-Olds (North Dakota) Sherburne County (Minnesota) Big Brown (Texas)	0-5.7	Total change in particle volume	Hegg and Hobbs (1980)
Smelters			
INCO Nickel (Copper Cliff, Canada)	0-7	Particulate sulfur to total sulfur ratio	Lusis and Wiebe (1976)
INCO Nickel (Copper Cliff, Canada)	1.2-5.2	Particulate sulfur to total sulfur ratio	Forrest and Newman (1977)
MT ISA Mines (MT ISA, Australia)	0.25[c]	Particulate sulfur to lead ratio	Roberts and Williams (1979)
Urban			
Los Angeles (California)	1.2-13	Particulate sulfur to total sulfur ratio	Roberts and Friedlander (1975)
St. Louis (Missouri)	7-12.5	Particulate sulfur to total sulfur ratio	Alkezweeny and Powell (1977)
St. Louis (Missouri)	3.6-4.2	Particulate sulfur to total sulfur ratio	Chang (1979)

[a] Adapted in part from Hegg and Hobbs (1980)

[b] Cloud condensation nuclei

[c] Diurnal average rate

The rates of SO_2 oxidation in industrial plant plumes consistently range from 0 to 10 percent/h, with urban plumes showing only a slightly greater maximum rate of 13 percent/h. The pre-1975 studies (Gartrell et al., 1963; Dennis et al., 1969; Weber, 1970; and Stephens and McCaldin, 1971), which observed conversion rates an order of magnitude larger than more recent observations, are suspect due to possible artifact formation in the sulfate analysis technique and limitations in the analytical methods in general.

Newman (1980) reviewed the majority of the power plant and smelter plume studies presented in Table 6-1 and arrived at the following conclusions:

1. The diurnal average oxidation rate of SO_2 to sulfate is probably less than 1 percent/h.
2. Little or no oxidation of SO_2 occurs from early evening to early morning.
3. Maximum oxidation rates of SO_2 to sulfate of 3 percent/h can occur under midday conditions.
4. The separate contribution of homogeneous and heterogeneous mechanisms to SO_2 oxidation in plumes cannot be deduced from the present studies.

The reported SO_2 oxidation rates are estimates based on analyses of measured physical and chemical parameters and in many instances have incorporated certain simplifying assumptions that are not totally substantiated. Also, present understanding of SO_2 chemical transformation processes indicate that SO_2 oxidation rates can vary significantly as a result of differences in the composition of source plumes and the air masses into which the plumes enter. Typical experimental uncertainties in measured SO_2 oxidation rates reported in Table 6-1 are 50 percent, but may be greater if inappropriate assumptions have been used. Even with these uncertainties, the overall consistency in the observed range of SO_2 oxidation rates is gratifying.

6.3 PHYSICAL REMOVAL PROCESSES

The removal of PM and gases from the atmosphere generally occurs through two physical processes: (1) dry deposition--the removal of chemical species from the atmosphere at the air-surface interface; and (2) precipitation scavenging--the removal of chemical species from the atmosphere by interaction with various types of precipitation such as rain, snow, etc. These processes have both a positive and negative impact on environmental air pollution issues. On one hand, they constitute the major mechanisms by which the polluted atmosphere cleanses itself, lowering ambient air concentrations of pollutant species and thereby reducing health-related risks. On the other hand, the deposited pollutant materials may constitute increased risks to our terrestrial and aquatic ecosystems.

Since wet and dry removal processes significantly affect the lifetime of SO_2 and PM in the atmosphere and thereby affect the distance traveled and the concentration of these species, understanding these processes is essential for a proper assessment of their environmental significance. The removal of pollutant species by dewfall has not been studied, and it remains for future research to determine whether this process is an important removal mechanism for atmospheric contaminants.

In the sections to follow, dry deposition and precipitation scavenging are discussed with emphasis on experimental data bases and theoretical treatment.

6.3.1 Dry Deposition

Sehmel (1980), McMahon and Denison (1979), Chamberlain (1980), and Garland (1978) reviewed particle and gas dry deposition. The dry deposition of SO_2 and PM, like other atmospheric species, is governed by three major components: meteorological variables, properties of the depositing pollutant, and surface variables. These components are influenced by specific parameters that interact in complex ways, which in many instances are not completely understood.

The most important meteorological processes affecting dry deposition are transport-related phenomena, which are governed by the wind and temperature profiles; eddy diffusion; and sedimentation across the boundary layer to the vegetation canopy or the surface. Two meteorological parameters strongly influence these processes: the friction velocity (u_*) and the aerodynamic surface roughness (z_0). Both of these parameters are used to describe the windspeed profile above a given surface under given conditions of atmospheric stability. Typically, these two variables are determined empirically by fitting optimal curves to windspeed data as a function of height. The strong diurnal dependence of dry deposition is linked to the formation of a stable layer of air at the earth's surface at night (nocturnal inversion) that effectively inhibits the vertical transport of pollutant species to the canopy or the surface. The formation of the nocturnal inversion and its effect on other atmospheric processes is discussed in the section on transport and diffusion.

Solubility in water is an important property influencing the dry deposition of a pollutant. Other important characteristics of PM are size distribution, density, morphology, and composition. Among the important surface properties are: (1) the moisture content of the surface which, in conjunction with the solubility of the pollutant species, govern the overall sticking efficiency of the deposited material; and (2) the physiological state of the vegetation surface, especially the opening and closing of stomatal pores, where the rate of pollutant uptake is thought to be strongly governed.

Chamberlain and Chadwick (1953) introduced a convenient way to express the rate of dry deposition of both gases and particles in terms of velocity. Dry deposition velocity (V_g) (defined as the downward flux (F) of the species, divided by its ambient concentration (x) at some specified height [typically 1 to 2 meters above the surface]), is the standard form in which all measured deposition rates are reported. Dry deposition velocities typically are reported in units of cm sec^{-1}.

$$v_g = \frac{-F}{x}$$

Dry deposition velocity is positive by convention and therefore requires a minus sign on F, the downward flux, which is defined as negative.

Hicks et al. (1980) reviewed and evaluated the measurement techniques for the dry deposition of pollutant species. They sorted measurement methods into three major categories: (1) estimates of accumulation, (2) flux monitoring, and (3) flux parameterization.

Though none of the experimental techniques has proven to be useful in all dry deposition measurements, a general consensus has been reached on the overall accuracy of the methods and their suitability for specific applications. Based on Hicks et al. (1980), the three categories are described briefly, with general comments on their limitations.

Estimates of accumulation may be considered using atmospheric radioactivity or mass balance methods. Radioactive techniques compare ambient concentrations of selected radioactive species with concentrations in water bodies, vegetation, etc., to evaluate the rate at which material enters the ecosystem over long periods. The technique generally is limited to small particle uptake of long-lived species and has difficulty distinguishing between dry and wet removal and resolving short-term variations. Mass balance studies attempt to measure the various inflow and outflow processes in the ecosystem, with the exception of dry deposition, which is then determined through a budget calculation. The method's major limitation is that dry deposition is inferred by indirect measurements, which in themselves are difficult to make accurately.

Flux monitoring considers the direct measurement of total deposition over a well-defined surface for set periods. Several types of deposition surfaces have been used with this general category, including open pots, flat filters, flat plates and shallow pans, fiber filters, and sticky films. Overall, the methods are limited due to their lack of standardization, dissimilarity to natural surfaces, and potential for contamination by locally resuspended particles.

Flux parameterization includes a variety of methods, one of which, eddy correlation, shows promise as a measurement standard for dry deposition of gases. Eddy correlation requires the simultaneous measurement of the concentration of pollutant species and the vertical component of the wind velocity at a sufficiently fast rate to determine the turbulent flux of the pollutant. The lack of adequate fast-response instruments for many of the pollutant species of interest significantly limits the technique. In addition, particle flux due to gravitational settling is not detected, and this can produce invalid results if significant particle resuspension occurs. Laboratory methods, including chamber and wind tunnel studies are also considered under the flux parameterization category. In these controlled experimental studies, plants, leaves, simulated canopy surfaces, etc., are exposed to known pollutant concentrations. Measurements of the change in concentration, which can be accomplished by a variety of methods, are then used to determine pollutant uptake.

6.3.1.1 Sulfur Dioxide Dry Deposition--The dry deposition of SO_2 onto grass, crops, forests, soil, and building surfaces has been reviewed by Sehmel (1980), McMahon and Denison (1979), Chamberlain (1980), and Garland (1978). McMahon and Denison (1979) presented compilations of dry deposition laboratory and field measurements of SO_2. A review of these results indicates measured dry deposition velocities ranging from 0.04 to 3.7 cm sec^{-1}, but with the majority in the range from 0.3 to 1.6 cm sec^{-1}. The apparent wide range of dry deposition values is not particularly disconcerting when the variety of surfaces, meteorological conditions, and experimental methods are considered. Table 6-2 summarizes the average dry deposition velocity by surface type.

TABLE 6-2. AVERAGE DRY DEPOSITION VELOCITY OF SO_2 BY SURFACE TYPE

Surface	Laboratory measurement, v_g(cm sec^{-1})	Field measurement, v_g(cm sec^{-1})
Alfalfa	1.2 (2)	1.6 (2)
Grass	--	1.1 (14)
Wheat	--	0.4 (3)
Forest	--	1.4 (5)
Sandy Soil	0.6 (2)	--
Clayey Soil	0.8 (2)	--
Soil	--	1.2 (4)
Land	--	1.2 (4)
Water (Fresh)	--	1.1 (6)
Ocean	--	0.5 (2)
Snow	--	0.3 (2)

Note: Values in parentheses indicate the number of separate studies used to obtain the average deposition velocity.

Source: McMahon and Denison (1979).

After reviewing the same set of data, Garland (1978) concluded that the mean deposition velocities for SO_2 over surfaces ranging from water and soil through short grass to forest were very similar and suggested that a value of about 0.8 cm sec^{-1} was applicable to large areas of Europe.

In a more detailed effort to estimate dry deposition velocities of SO_2 and particulate sulfate over the eastern half of the United States, southern Ontario, and nearby oceanic regions, Sheih et al. (1979) computed deposition velocities as a function of land use characteristics, surface roughness scale lengths, and surface resistances to pollutant uptake. Gridded dry deposition velocity maps of sulfur dioxide and sulfate corresponding to half degree increments of longitude and latitude were computed for a range of atmospheric stabilities. The results indicate that deposition velocity distributions for SO_2 are not uniform for the less stable atmospheric conditions. For very unstable atmospheric conditions (Pasquill category A) dry deposition velocities over the eastern United States ranged from 0.4 to 0.9 cm sec^{-1} (excluding water surfaces) for SO_2, with a mean areawide dry deposition velocity of approximately 0.6 cm sec^{-1}. Under the same conditions, the deposition velocity for sulfates ranged from 0.7 to 0.9 cm sec^{-1} with a mean value of approximately 0.8 cm sec^{-1}. Sheih et al. (1979) noted that, under nearly calm conditions at night, stability classification schemes do not adequately represent the nocturnal inversion formed at the surface and recommend that a dry deposition velocity of 0.07 cm sec^{-1} be assumed for both SO_2 and sulfate particles.

6.3.1.2 Particle Dry Deposition--As a measurement for pollutant species of interest, the dry deposition of particulate matter is less understood. In Sehmel (1980) and McMahon and Denison (1979), deposition velocities for particle species are compiled for both artificial and natural surfaces. Unfortunately, with the exception of lead particles from automotive exhaust, virtually no data exist for other particulate pollutants, such as sulfates, nitrates, and carbon-containing particles. The interpretation of the relationship between deposition measurements with fallout collectors and dry deposition rates on natural surfaces creates an additional problem. Fallout collectors, which were used in a significant portion of the measurements reported, generally do not have the characteristics of the surfaces they are attempting to simulate.

Tables 6-3 and 6-4 from the study by McMahon and Denison (1979) compile literature values for the deposition velocities of particles measured under laboratory and field conditions, respectively. The data cover a range of surface variables, particle sizes and composition, and meteorological conditions. A review of the data indicates:

1. Deposition in nature varies considerably through processes that are not totally understood.
2. The minimum deposition velocity for particles occurs at diameters from 0.1 to 1.0 μm.
3. Deposition velocities are often reported for particle diameters and size distributions that do not reflect typical atmospheric PM characteristics.

The experimental uncertainties associated with particle dry deposition velocity measurement have stimulated the development of theoretical models for simulating the dry deposition process and predicting dry deposition velocities given specific meteorological data (Sehmel, 1980; Slinn, 1978, 1977; Davidson and Friedlander, 1978). The models describe only the physical processes of bringing the particle to the depositing surface. Particle shapes other than spherical, particle composition, or surface properties have not been considered with regard to particle retention. Particle size, an important property in the aerodynamic flow of particles to surfaces, is considered in these studies. The typical model result shows that predicted deposition velocities increase as surface roughness and/or friction velocity increases and are nearly independent of atmospheric stability. The deposition velocity for particles passes through a minimum in the 0.1 to 1 μm diameter particle range. Figure 6-2 (Sehmel, 1980) presents deposition velocities predicted by one model at 1 m from the surface, for $u_* = 30$ cm sec^{-1} and particle densities of 1, 4, and 11.5 g/cm^3.

Table 6-5 shows the range of predicted deposition velocities at a height of 1 m for two particle size regions and for a range of aerodynamic surface roughness lengths, mean windspeeds, and calculated friction velocities. These results are based on the model of Sehmel (1980) and should be representative of most meteorological and surface conditions.

TABLE 6-3. LABORATORY MEASUREMENTS OF DEPOSITION VELOCITIES OF PARTICLES

Author (date)	v_g (cm sec^{-1})	Reference height (m)	Particle diameter (μm)	Surface	Comment
Chamberlain (1967)	0.03 0.03 0.1 0.8		0.1 1 2 5	Grass	--
Möller and Schumann (1970)	$v_g \propto D^{2/3}$				D = diffusion coefficient $2 \times 10^{-2} \geq D \geq 2 \times 10^{-3}$ cm^{2}sec^{-1}
Chamberlain and Chadwick (1972)	$v_g = 0.06\ u_*$ $v_g = 0.12\ u_*$		20-30	Cereal crops	Dry Includes wind tunnel Wet and field data
Clough (1973)	0.005 0.003 0.3 2	0.1	0.08 0.5 5 20	Filter paper	v_g to copper also measured v_g found to be a function of windspeed
Sehmel (1973)	2×10^{-3}-10	0.01	0.1-28	Smooth brass	--
Sehmel and Sutter (1974)	5×10^{-3}-29	0.01	0.2-30	Water	--
Belot and Gauthier (1975)	$v_g \propto u^3$ $v_g \propto d^4$		1-10	Shoots of pine and oak trees	u = wind speed d = particle diameter
Klepper and Craig (1975)	0.0035		0.8	Bean leaves	--
Craig et al. (1976)	0.01		0.1 1	Smooth	Wind tunnel
Wedding et al. (1976)					Deposition rate on pubescent leaves of sunflower was nearly 7 times that of the non-pubescent leaves of tulip poplar.

TABLE 6-3. (continued)

Author (date)	v_g (cm sec^{-1})	Reference height (m)	Particle diameter (μm)	Surface	Comment
Little and Wiffen (1977)	0.11		5×10^{-2}	Short grass	--
	0.02		0.2		
Little (1977)	0.5		2.75	Nettle	These data are for whole shoots for wind speeds of 2.5 m sec^{-1}. Data for other wind speeds and separate plant surfaces are given in reference.
	0.04			Beech	
	0.3			White Poplar	
	0.9		5	Nettle	
	0.1			Beech	
	0.3			White Poplar	
	1.5		8.5	Nettle	
	0.3			Beech	
	0.8			White Poplar	

Source: McMahon and Denison (1979).

TABLE 6-4. FIELD MEASUREMENTS OF DEPOSITION VELOCITIES OF PARTICLES

Author (date)	v_g (cm sec^{-1})	Reference height (m)	Particle composition	Surface	Comment
Chamberlain (1953)	2.1	0.3-0.9	16 μm*	Grass	u = 9.2 m/sec
	1.1	0.3-0.9	16 μm*		u = 3.2 m/sec
	0.5	0.3-0.9	16 μm*		u = 1.1 m/sec
Eriksson (1959)	0.7			Ocean	Chloride over Scandinavia
	1.6			Land	--
Small (1960)	0.5 (0.2-3.4)			Land	Radioactive particles over Norway
Neuberger et al. (1967)			Ragweed	Coniferous forest	80 percent ragweed pollen removed from air by forest
White and Turner (1970)	5.6		Na	Mixed deciduous woodland	1. Probable overestimation of aerosol income, hence v_g. 2. Standard deviation varied between 65 and 95 percent of mean v_g.
	4.7		K		
	3.0		Ca		
	7.1		Mg		
	0.8		P		
Esmen and Corn (1971)	$v_g = 0.50$		0.1-10 μm*	Filter paper Millipore filter Glass slide	--
Chamberlain and Chadwick (1972)	$v_g = 0.06\ \mu_\star$		20-30 μm*	Cereal crops	Dry } Includes wind tunnel and field data.
	$v_g = 0.12\ \mu_\star$				Wet }
Pierson et al. (1973)	0.1-0.6			Land	v_g estimated for 23 trace elements based on several years of data

TABLE 6-4. (continued)

Author (date)	v_g (cm sec^{-1})	Reference height (m)	Particle composition	Surface	Comment
Cawse (1974)	1.3		Al		Extracted from Gatz (1975). Values in parentheses were estimated by Gatz from a relationship between particle size and v_g.
	0.22		As		
	(0.45)		Cd		
	0.50		Cr		
	(0.50)		Cu		
	1.1		Fe		
	0.56		Mn		
	(0.45)		Ni		
	0.30		Pb		
	(1.0)		Ti		
	0.29		V		
	0.62		Zn		
Hart and Parent (1974)			Na, Ca, Mg, K, P, NO_3	Douglas fir and junipers	Deposition ratio: $\frac{\text{beneath trees}}{\text{open terrain}} = 3\text{-}16$
Clough (1975)	3.4			Grass	Dry $u_* = 37$ cm sec^{-1}
	7.3			Grass	Dry $u_* = 87$ cm sec^{-1}
	11		30 μm*	Grass	Wet $u_* = 87$ cm sec^{-1}
	61			Dry moss	
	100			Wet moss	
	0.74		4 μm*		
	1.1			Grass	Dry $u_* = 37$ cm sec^{-1}
	0.75		3 μm*	Grass	
	12.7			Dry moss	Dry $u_* = 37$ cm sec^{-1}

*particle diameter

TABLE 6-4. (continued)

Author (date)	v_g (cm sec^{-1})	Reference height (m)	Particle composition	Surface	Comment
Abrahamsen et al. (1976)			SO_4^{-2}	Spruce and pines	Deposition ratio: $\frac{\text{beneath trees}}{\text{open terrain}} = 2$
Dovland and Eliassen (1976)	0.16 0.68		Atmospheric aerosol	Snow	Lead SO_4^{-2} : upper bound value
Fritschen and Edmonds (1976)	0.07 0.46		3 μm*	Douglas fir	
Prahm et al. (1976)	0.4		Atmospheric aerosol	Atlantic ocean	SO_4^{-2}
Krey and Toonkel (1977)	0.5				^{90}Sr : HASL wet-dry collector
Wesley et al. (1977)	0.6	5	0.05-0.1 μm*	Bare soil and grass	$u < 2$ m sec^{-1}: Eddy correlation method.

Source: McMahon and Denison (1979).

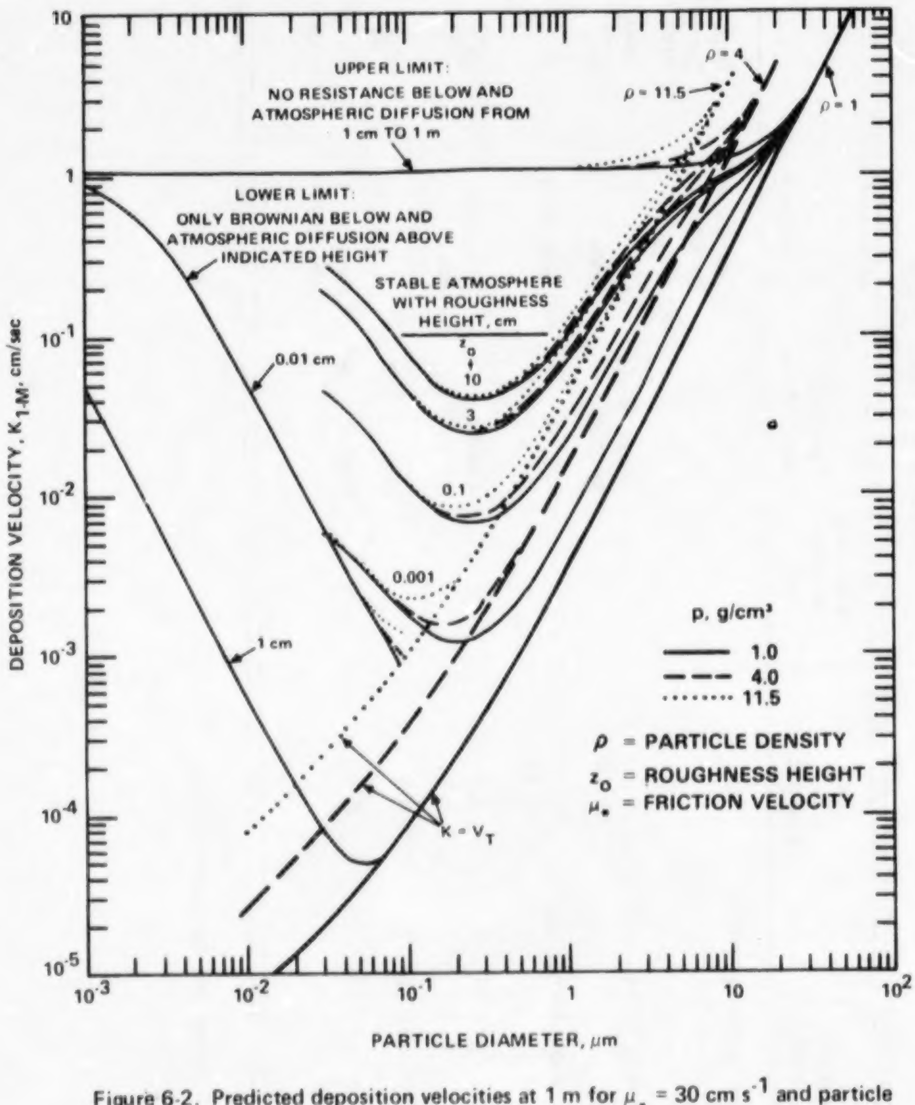

Figure 6-2. Predicted deposition velocities at 1 m for $\mu_* = 30$ cm s^{-1} and particle densities of 1, 4, and 11.5 g cm^{-3}.

Source: Sehmel (1980).

TABLE 6-5. PREDICTED PARTICLE DEPOSITION VELOCITIES[a]

Z_o cm	$u/u_\star$ m sec^{-1}/cm sec^{-1}	Deposition Velocity Range[b] Particle Diameter 0.1 to 1 μm cm sec^{-1}	Deposition Velocity Range[b] Particle Diameter 1 μ to 10 μm cm sec^{-1}
0.1	2.3/10	$1.5\times1\text{-}^{-2}$ - 5.0×10^{-2}	5.0×10^{-2} - 4
10	1.2/10	9.0×10^{-2} - 1.5×10^{-1}	1.5×10^{-1} - 4
0.1	11.5/50	2.0×10^{-2} - 5.5×10^{-2}	5.5×10^{-2} - 4
10	5.8/50	1.0×10^{-1} - 2.0×10^{-1}	2.0×10^{-1} - 4

[a] Based on model predictions in Sehmel (1980)

[b] Particle density of 11.5 g/cm^3

6.3.2 Precipitation Scavenging

As with dry deposition, precipitation scavenging or wet removal results from a series of complex physical and chemical interactions involving properties of the scavenging media and the species removed. For the past 30 years, research in the area has focused on removing from the atmosphere radioactive debris introduced by nuclear weapons testing (Bowen, 1960; Engelmann, 1968; Volchok et al., 1971) and in conjunction with material balance or budget studies on the removal of various elemental species from the atmosphere (Robinson and Robbins, 1970; Rasmussen et al., 1975; Junge, 1972, 1974).

Engelmann (1968), Postma (1970), Hales (1972), Slinn et al. (1978) and Slinn (1981) have researched and reviewed the theory of precipitation scavenging. Though our understanding of the details of the complex processes operating in precipitation scavenging is incomplete, significant progress has been made in deducing the general scavenging pathways and in developing appropriate parameters for their quantitative treatment. As pointed out by Slinn (1981) and others, the removal of trace constituents from the atmosphere by precipitation scavenging depends on: (1) the position of the trace consitituent relative to the scavenging media; (2) the physical form of the scavenging media; (3) the chemical and physical properties of the trace constituent; and (4) the specific physical/chemical process that is operative. These basic factors are schematically illustrated in Figure 6-3.

A convenient practice in evaluation of precipitation scavenging is to distinguish between below-cloud and in-cloud scavenging processes. Unfortunately, use of the terms "rainout" for in-cloud and "washout" for below-cloud scavenging, has led to confusion. It is difficult to clarify the contribution of these processes to the total scavenging during precipitation. Washout, which is easier to study, has received more scientific attention. In many experimental studies, the distinction between the two processes has been ignored and only the total precipitation scavenging has been considered. The theoretical approaches discussed in the

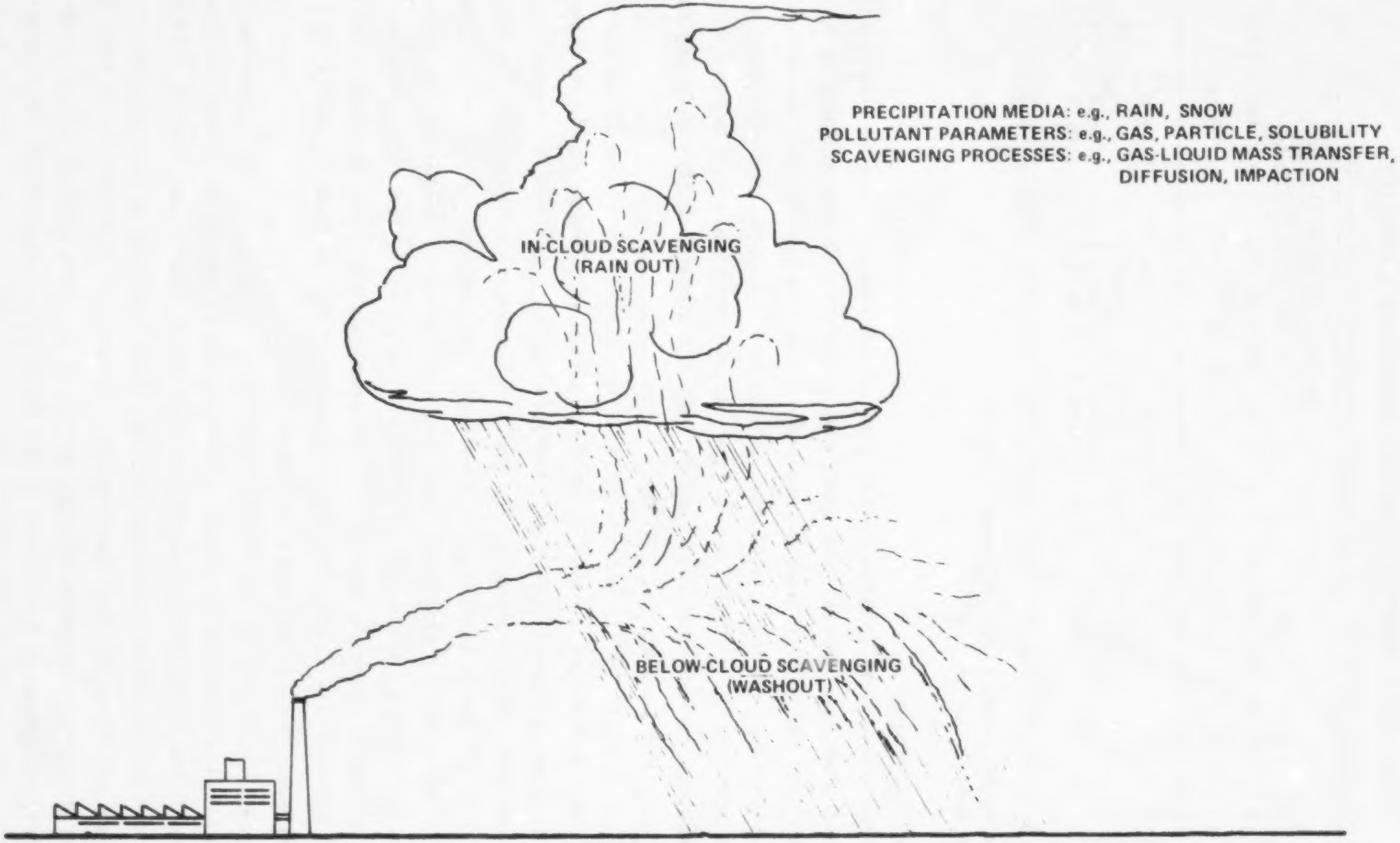
PRECIPITATION MEDIA: e.g., RAIN, SNOW
POLLUTANT PARAMETERS: e.g., GAS, PARTICLE, SOLUBILITY
SCAVENGING PROCESSES: e.g., GAS-LIQUID MASS TRANSFER, DIFFUSION, IMPACTION
IN-CLOUD SCAVENGING (RAIN OUT)
BELOW-CLOUD SCAVENGING (WASHOUT)

Figure 6-3. Basic factors influencing precipitation scavenging.
Source: Adapted from Slinn (1981).

following section are for washout processes only, while the empirical parameterizations consider total gas and particle scavenging.

The parameterization of the precipitation scavenging process has generally taken the form of a loss rate per unit volume and has evolved from various assumptions applied to the continuity equation (Slinn, 1977). Parameterizations for the removal of gases by rain and the removal of particles by rain and by snow are considered in the following sections. The formalism and technical rigor used in their development are discussed elsewhere (Hales, 1972, 1978; Slinn, 1977) and are beyond the scope of the present discussion.

6.3.2.1 Sulfur Dioxide Wet Removal--The removal of SO_2 from the atmosphere by rain is governed by basic physical processes of absorption and desorption of the SO_2 molecules from the hydrometeor (Hales, 1972, 1978) and by a series of chemical reactions (Postma, 1970; Hill and Adamowicz, 1977; Barrie, 1978) that account for the liquid phase oxidation of SO_2. As a physical process, the rate of scavenging of a gas by rain is a function of the size spectrum of the rain droplets, the fall path of the rain droplet to the ground, the rainfall rate, and the solubility of the gas. Hales (1978) and Slinn et al. (1978) developed general expressions for computing the scavenging of SO_2 and other gases, given simplifying assumptions on the character of the precipitation and solubility of the gas. As pointed out in Chapter 2, the liquid phase oxidation of SO_2 is complex and not thoroughly understood. The uptake of SO_2 by rain droplets proceeds through the dissolution of SO_2 and a subsequent series of dissociation reactions. The chemical equilibria and associated reaction rates for the dilute sulfur dioxide-pure water system are well known and the reactions sufficiently fast that thermodynamic equilibrium between gas phase and liquid droplet phase can be assumed. Therefore, the physical dissolution of SO_2 in rain droplets follows a Henry's Law relationship that predicts reversible absorption to a degree that depends on the physical and chemical state of the rain droplet and the ambient atmosphere through which it travels (Hales, 1972). Treatment of these processes is relatively straightforward, but there is uncertainty in the SO_2 wet removal process because of the effect of trace substances on the SO_2 dissociation equilibria and the effective oxidation rate of SO_2 in solution. In this light, several recent studies by Hill and Adamowicz (1977), Barrie (1978), Garland (1978), and Gravenhorst et al. (1978) have considered the SO_2-bisulfite oxidation process in predicting wet removal rates of SO_2 under various atmospheric conditions.

Barrie (1978) modeled the washout of SO_2 from a plume under varying meteorological and SO_2 concentration conditions. He assumed that SO_2 oxidation in the raindrops could be neglected due to the limited time for reaction (0 to 5 min), the low pH's encountered (Beilke et al. 1975), and the dissolution of the SO_2 governing pH of the raindrop. He concluded that the fractional plume washout rate (percent/mm rain) is inversely related to the plume concentration and thickness. That is, for a given precipitation rate, the plume washout rate (percent/h) increases with decreasing plume concentration or decreasing plume thickness. For heavy rain (25 mm/h), washout from a 1000 ppb(v) SO_2 plume of 20 m thickness occurs at a rate of 56 percent/h, while under drizzle conditions (0.5 mm/h) for a 300 ppb(v) SO_2 plume of 50 m thickness the rate was 2 percent/h.

In a more explicit treatment of SO_2 washout, Hill and Adamowicz (1977) accounted for the effects of SO_2 oxidation within rain droplets and of the pH of precipitation on the SO_2 washout process. They indicated that pH can be quite variable (over six orders of magnitude in hydronium ion concentration, equivalent to six pH units) at SO_2 ambient levels of 10 ppb and less. As SO_2 levels increase, the variability in background pH decreases. The SO_2 oxidation rate of 3.6 percent/h used in the calculations is based on the catalytic oxidation studies of Brimblecombe and Spedding (1974). In a typical calculation of the rate of SO_2 washout, Hill and Adamowicz (1977) assumed various ambient SO_2 concentrations, well mixed through a layer 1 km in depth, and a rainfall rate of 1 mm/h, with a predominant drop radius of 0.5 mm and a pH of 7. Calculated washout rates of SO_2 under these conditions were 2.6 percent/h and 0.8 percent/h for ambient SO_2 levels of 10 ppb and 100 ppb (30 and 260 μg/m^3), respectively.

A convenient empirical expression for the wet removal of gases takes the form of an exponential decay process, where the time constant for decay (scavenging coefficient for the gas), determined in field and laboratory studies, is a function of the rainfall intensity. The expression takes the form

$$\chi_t = \chi_o e^{(-\Lambda_g t)}$$

where χ_t and χ_o are the atmospheric concentrations of the gas at time t and zero, respectively, and Λ_g is the scavenging coefficient for the gas. Chamberlain (1953), Beilke (1970), Hales et al. (1971), Dana et al. (1975) and others have reported estimates of the scavenging coefficient for sulfur dioxide. Calculated scavenging rates of SO_2 using these coefficients can range typically from 2 percent/h to 22 percent/h.

6.3.2.2 Particle Wet Removal--The study of precipitation scavenging of particles has focused on theoretical studies (Slinn, 1977; Grover et al., 1977; Wang et al., 1978), but emphasis in experimental work has taken hold in recent years (Dana and Hales, 1976; Radke et al., 1980; Gatz, 1977). The wet removal of sulfate PM in the ambient environment has been of particular interest (Scott, 1978; Hales, 1978; Dana, 1980) due to the acidity of many of these particles and the increased concern for the phenomenon termed "acid rain." Acidic precipitation and its associated scientific issues are discussed in Chapter 7.

As with gases, the size spectrum of the rain droplets, the fall path of the rain droplet to the ground, and the rainfall rate, as well as the size distribution and composition of the particulate matter affect the particle scavenging rate by precipitation. Slinn (1977) developed general expressions for computing the scavenging of particles given certain simplifying assumptions, as has been done with gases.

A practical approach in predicting the wet removal of particles, as mentioned previously for gases, has been through the measurement of empirical scavenging coefficients. McMahon and Denison (1979) compiled a comprehensive list of field measurements of wet scavenging coefficients of particles, which is presented in Table 6-6. A cautionary note is in order.

TABLE 6-6. FIELD MEASUREMENTS OF SCAVENGING COEFFICIENTS OF PARTICLES

Author (date)	Λ_p (sec^{-1})	Particle composition	Comment	
Kalkstein et al. (1959)	2×10^{-5} 2×10^{-5}	SO_4^{-2}, NH_4^+ Cl, NO_3	Rainout Washout	As calculated by Makhon'ko (1967)
Georgii (1963)	4×10^{-5} 22×10^{-5} 4×10^{-5}	Dissolved inorganic contaminant	Rainout Washout	
Banerji and Chatterjee (1964)	0.4×10^{-5}	Radon	Rainout	As calculated by Makhon'ko (1967)
Makhon'ko (1964)	2×10^{-5} $\leq 1 \times 10^{-5}$	Fission products	Rainout Washout	
Shirvaikar et al. (1960)	7×10^{-5}	Atmospheric dust	Rainout	As calculated by Makhon'ko (1967)
Makhon'ko and Dmitrieva (1966)	20×10^{-5}	Fission products	Rainout	
Makhon'ko (1967)	7×10^{-5}	Atmospheric dust	Rainout plus washout	
Wolf and Dana (1969)	0.5×10^{-5} J	0.5 µm*	Snowout, see also Knutson and Stockham (1977)	
Bakulin et al. (1970)	3×10^{-5}		^{212}Pb; washout from thunderstorm	
Burtsev et al. (1970)	$15 \times 10^{-5}\ J^{0.5}$ $20 \times 10^{-5}\ J^{0.5}$	≈0.2 µm* ≈0.2 µm*	Washout Rainout	
Dana (1970)	13×10^{-5} J	7.5,3 µm*	Uranine and rhodamine particles respectively	
Perkins et al. (1970)	300×10^{-5}	Atmospheric aerosol	Rainout	
Peterson and Crawford (1970)	$16 \times 10^{-5}\ J^{0.5}$	5 µm*	Based on Engelmann's data (1965)	
Esmen (1972)	0.4×10^{-5}	Atmospheric aerosol	Includes rainout	

TABLE 6-6. (continued)

Author (date)	Λ_p ($\sec^{-1}$)	Particle composition	Comment
Rodhe and Grandell (1972)			Suggest Λ proportional to rainfall intensity
Acres-AESC (1974)	0.7×10^{-5}	Atmospheric aerosol	Includes rainout
Graedel and Franey (1975)	$\Lambda_{snow} = 25\text{-}50\Lambda_{rain}$	0.4-1 μm*	See Slinn (1976)
Hicks (1976)	50×10^{-5}	< 1 μm*	Rainout
Graedel and Franey (1977)	19×10^{-5}		Condensation nuclei
	18×10^{-5}	0.3-0.5 μm*	
	28×10^{-5}	0.5-0.7 μm*	
	43×10^{-5}	0.7-0.9 μm*	Snow
	65×10^{-5}	0.9-1.5 μm*	
	92×10^{-5}	1.5-3 μm*	
Radke et al. (1977)			See Fig. 6.4

J = rainfall intensity in mm/h

*particle diameter

Source: McMahon and Denison (1977).

The scavenging coefficients are dependent on the rainfall rate, the mean raindrop radius, and the particle size. When these factors are considered, the scavenging coefficients reported in Table 6-6 show reasonable consistency, as demonstrated by Figure 6-4.

Airborne measurements by Radke et al. (1980) on precipitation scavenging of aerosol particles greater than 0.01 μm diameter in aged air masses, coal-fired power plant plumes, a kraft paper mill, and a plume from a volcanic eruption supported theoretical estimates of wet removal for aerosol particles greater than 1.0 μm. Marked differences were observed in the submicrometer particle region, where measured scavenging efficiencies for submicrometer aerosol particles were typically an order of magnitude greater than theoretical predictions. The scavenging gap, that portion of the aerosol particle size range where scavenging collection efficiencies are at a minimum, was narrower than theoretically predicted. Radke et al. (1980) offer some explanations for the discrepancies, including deliquescent growth and nucleation scavenging of the submicrometer particles in convective clouds. Considering the varied aerosol particle sources and precipitation studied, the measurements showed marked continuity (see Figure 6-5).

6.4 TRANSPORT AND DIFFUSION

Pollutant substances emitted into the atmosphere are transported and diffused as a result of a series of complex physical interactions that result in the mean motion of air and its fluctuating components. Transport and diffusion are associated with spatial and temporal scales. The spatial or temporal domain directly influences what specific physical phenomena will most affect transport and diffusion.

Studies of air pollution transport and diffusion fall broadly into two categories, depending on the extent of the horizontal scale studied. High pollutant concentrations that occur in the vicinity of a major emission source are dominated by physical processes that operate on a local horizontal scale of the order of 1 to 5 km, or approximately 1 hour of transport. Since the majority of criteria pollutants are emitted directly into the atmosphere by major sources, this has been the primary area of interest in air pollution regulation. However, as air pollution issues are raised with regard to pollutants of a more ubiquitous nature that have appreciably longer lifetimes and, in some cases, form through secondary reaction processes, the horizontal scale of interest expands considerably. Sulfur dioxide and particulate matter span a horizontal scale ranging from local to global. A brief review of the physical processes contributing to transport and diffusion is presented in Section 6.4.1, while Section 6.4.2 considers residence times of pollutants and their long distance transport.

6.4.1 The Planetary Boundary Layer

The mean wind within approximately the first 1000 meters above the earth's surface carries most of the pollutants within the atmosphere. The mean wind is determined primarily by the interaction of three forces governed by thermodynamic and mechanical processes: (1) the force due to the horizontal pressure gradient produced by differential solar heating of the

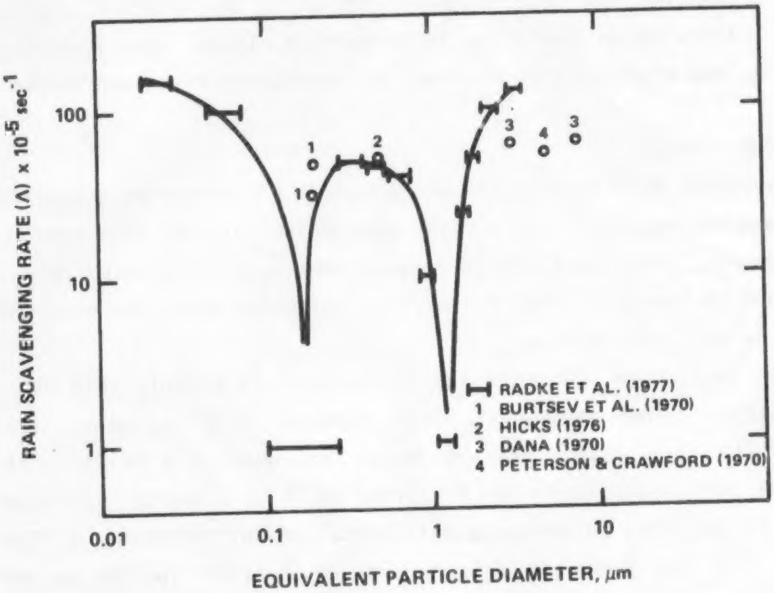

Figure 6-4. Relationship between rain scavenging rates and particle size.

Source: McMahon and Denison (1979).

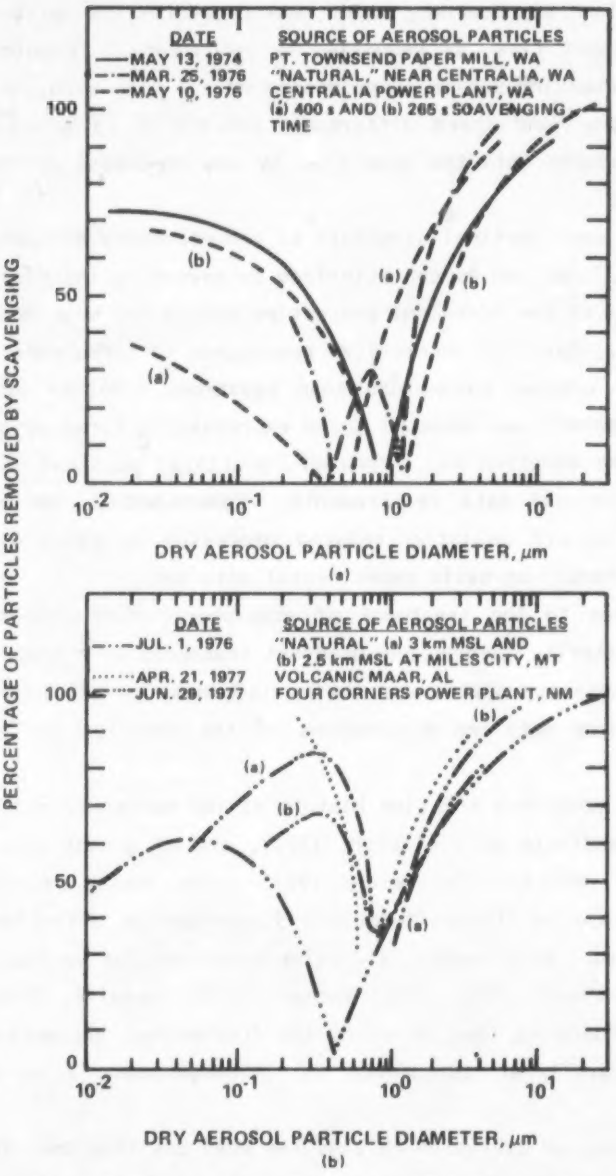

Figure 6-5. Percentages of aerosol particles of various sizes removed by precipitation scavenging.

Source: Radke et al. (1980).

earth's surface; (2) the Coriolis force due to the earth's rotation; and (3) the friction force due to the texture of the earth's surface. The planetary boundary layer is that portion of the atmosphere within which surface frictional effects have a substantial impact on the mean wind. Typically, this layer is hundreds of meters deep and varies diurnally.

Diffusion in the planetary boundary layer, which governs the spreading of pollutants perpendicular to the transport flow, is regulated by turbulence. Turbulence, which comprises a complex spectrum of fluctuating motion superimposed on the mean wind, is generated through the interaction of directional and speed differences (shear) in large-scale atmospheric motions and perturbations introduced into the mean flow by the roughness of the earth's surface, as well as by solar heating.

The theory of the mean vertical structure of the planetary boundary layer is fairly well understood (Haugen, 1973) and can be characterized by measuring the basic meteorological parameters. The description of the turbulent properties within the mean motion, which govern diffusion, is more elusive. Detailed theoretical approaches to turbulence are difficult to solve because they have more unknown parameters than equations. Higher order closure techniques apply assumptions that permit new unknowns to be expressed in terms of others in such a way as to allow solution of the equation set. However, practical application is limited because of their intensive computer and data requirements. Consequently, the practical treatment of atmospheric diffusion to air pollution-related processes is based on highly parameterized theories that depend strongly on basic experimental data sets.

Practical approaches to the treatment of atmospheric diffusion have been derived from statistical theory, similarity theory, and gradient transport or K-theory (Pasquill, 1974). A brief description of these approaches and their usefulness in air pollution-related problems is presented below. More detailed discussions of the theories can be found in the cited references.

Statistical theory considers the time history of the motion of a single fluid "particle," relative to a fixed coordinate axis (Taylor, 1921), and of groups or clusters of such particles relative to their centroid (Batchelor, 1953). The theory provides the basis for the development of the Gaussian diffusion formula and provides an effective means of correlating empirical dispersion data. As a result, diffusion equations for various emission source types have been developed (Gifford, 1968, 1975; Turner, 1970; Pasquill, 1974, 1975). A practical limitation of this approach is that it makes the fundamental assumption of turbulence homogeneity, whereas boundary-layer turbulence is inhomogeneous, especially in the vertical dimension.

The similarity theory of diffusion relates the mean position and other properties of diffusing clouds and plumes to the characteristic parameters of the surface layer, by dimensional reasoning. Results (Monin and Yaglom, 1971) are reasonably complete for the surface layer, but extension to the entire boundary layer introduces further parameters, which limits their practical use.

The gradient-transport, or K-theory, of diffusion is the oldest, originating with Fick (1855) and Boussinesq (1877). Atmospheric applications have been most successful at large scales, including global diffusion. At boundary-layer scales the behavior of K is quite complicated. Useful results can be obtained (Pasquill, 1974; Yaglom, 1975; Csanady, 1973), but the mathematics tend to be elaborate. The essential problem is to account for the strong space-time scale dependence of eddy-diffusivity, which was first demonstrated by Richardson (1926). Berlyand (1974) based a comprehensive system of air pollution analysis entirely on a form of K-theory.

Obukhov (1941) showed that the parameterization of atmospheric diffusion follows a form of Richardson's law of diffusion, where the total amount of turbulent energy dissipation and the pollutant spreading is proportional to the diffusion time to the 3/2 power. Data on the instantaneous values of the spreading of plumes and puffs (i.e., on relative diffusion) shows that this law describes diffusion up to t on the order of an hour (Gifford, 1976a). On the other hand, the time-average spreading of plumes was shown by Taylor (1921) to obey the asymptotic laws $\sigma \propto t$ (where σ = the standard deviation of the horizontal spreading of the pollutant cloud and t = time) for small t values and $\sigma \propto t^{1/2}$ in the limit of large t values. Diffusion depends both on travel time from source to receptor and on the sampling duration (i.e., the time over which the concentration is averaged at the receptor point). The situation is made more complicated by the fact that cross-wind diffusion exhibits markedly different behavior than vertical diffusion in the boundary layer because of the inhibiting effect on vertical turbulence fluctuations imposed by the presence of the ground and because of the strong damping effect of stability on vertical turbulent motions.

Numerous attempts have been made to relate horizontal and vertical boundary layer diffusion for flat uniform terrain, as measured by the lengths σ_y and σ_z, to more or less easily measured quantities that characterize boundary layer thermal and mechanical turbulence properties. Gifford (1976b) and Weber (1976) extensively surveyed the literature. Gifford stressed the common logic underlying various, sometimes seemingly conflicting, schemes as well as the need to evaluate many exceptional cases that arise in practical applications.

Based on these analyses and those of Pasquill (1975, 1976), the diffusion parameterization originally suggested by Pasquill (1961) is valid for sources located at or fairly near the surface, for uniform underlying terrain, and for receptors up to a distance of several kilometers. Greater distances, varying surface roughness, and other generalizations have been discussed (Smith, 1972) as well as relations to surface-layer turbulence parameters (Golder, 1972; Draxler, 1976). The difficulties of applying this method to practical air pollution problems center on cases for which the turbulence is produced or modified by factors that extend beyond the purely thermal and mechanical components that control the local boundary-layer turbulence.

6.4.2 Horizontal Transport and Pollutant Residence Times

The horizontal distance over which a pollutant is transported is strongly influenced by: (1) its overall lifetime or residence time in the atmosphere: (2) the characteristics of the mean wind; and (3) the time of day and height at which the pollutant is emitted into the atmosphere.

Residence times for pollutants are governed by the extent of wet and dry removal and chemical transformation the pollutant species undergoes in the atmosphere. Figure 6-6 estimates residence times for typical pollutants and their associated characteristic horizontal meteorological scale. Average windspeeds of 5 m/sec were assumed in approximating the distance scale. Residence time estimates are based on the work of Junge (1972, 1974).

Transport scales for pollutants such as SO_2, which have appreciable dry deposition velocities, are sensitive to the relative height at which the pollutant is emitted. Pollutant distributions are also sensitive to the stability of the atmosphere, which governs the extent of vertical mixing to the surfaces.

Industrial facilities emitting large quantities of SO_2 have tried to take advantage of these natural meteorological phenomena to reduce ambient levels of SO_2 in the vicinity of their stacks. By building taller effluent stacks, emitting facilities injected SO_2 at higher levels in the atmosphere, allowing the pollutant more time to be dispersed and transported before reaching ground level, thereby effectively reducing ground-level concentrations of SO_2. A great deal of controversy arose over whether this approach circumvents the intent of the Clean Air Act. As a result of the Clean Air Act Amendments of 1977, EPA requires that the degree of emission limitation necessary for control of any air pollutant cannot be achieved through the construction of stacks higher than would be considered appropriate using good engineering practice design standards. An interesting corollary of the tall stack issue is the potential for such sources to enhance the production of particulate sulfate. When SO_2 is emitted at higher levels in the atmosphere, the probability of its removal by dry deposition is lowered, thus extending its lifetime in the atmosphere and subsequently enhancing the probability of its being transformed to particulate sulfate through chemical reaction.

Of particular importance to horizontal transport is the strength and time of formation of the nocturnal inversion, a stable layer of air formed at the surface due to the differential cooling of the earth's surface relative to the night air. This stable layer varies in thickness from approximately 50 m to 500 m depending on meteorological conditions. At the onset of the nocturnal inversion, all pollutants present in the well-mixed layer from the day's emission are cut off from the surface by this stable layer of air. There are no major mechanisms for transport through this layer, so dry deposition processes virtually stop, leaving the pollutant reservoir aloft free to travel long distances with negligible losses. In addition, horizontal mean windspeeds are typically higher in layers aloft, due to the reduction in frictional drag at the earth's surface as a result of the presence of the stable nocturnal layer.

Associated with this overall process is a phenomenon of particular importance to nighttime transport, the nocturnal jet. According to Blackadar (1957), the nocturnal jet forms as a result of decoupling of winds previously restrained by frictional forces at the surface. These winds are now free to accelerate in response to existing pressure gradients. As a

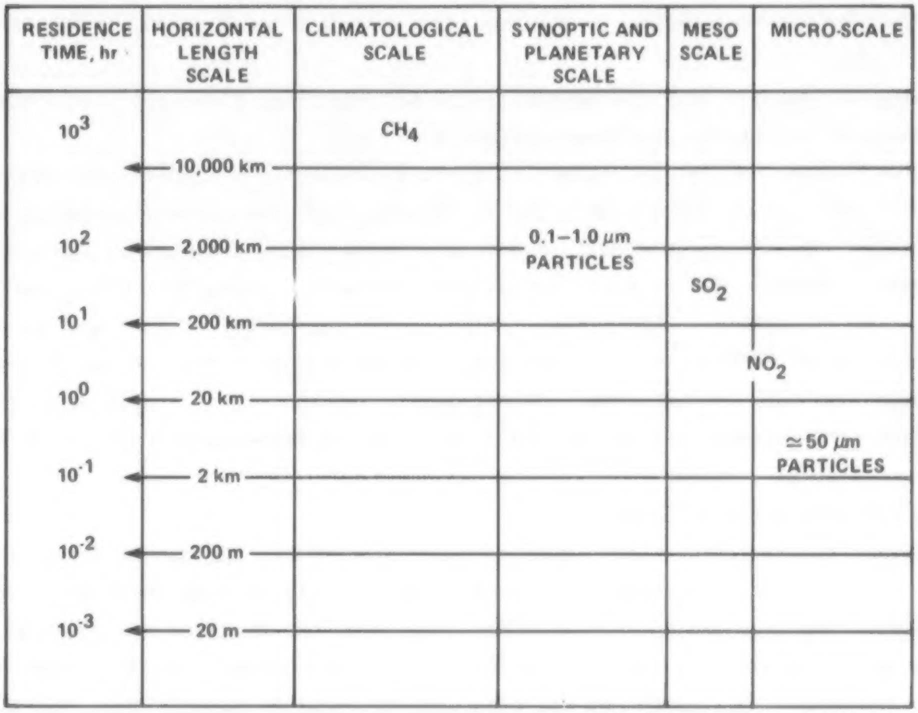
RESIDENCE TIME, hr
HORIZONTAL LENGTH SCALE
CLIMATOLOGICAL SCALE
SYNOPTIC AND PLANETARY SCALE
MESO SCALE
MICRO-SCALE
10^3
CH_4
10,000 km
10^2
2,000 km
0.1–1.0 μm PARTICLES
SO_2
10^1
200 km
NO_2
10^0
20 km
≃ 50 μm PARTICLES
10^{-1}
2 km
10^{-2}
200 m
10^{-3}
20 m

Figure 6-6. Estimated residence times for select pollutant species and their associated horizontal transport scale.

result, some overshooting in windspeed occurs as the flow attempts to establish a new balance with inertial forces. Bonner (1968) examined 2 years of upper-level wind data from the National Weather Service's rawinsonde network to determine the frequency and geographical distribution of the low-level jet. Recently, high-resolution measurements of wind profiles collected over central Illinois (Sisterson and Frenzen, 1978) showed that nocturnal, low-level wind maxima occur more frequently than indicated in Bonner's analysis. In these studies, made during the summers of 1975 and 1976, low-level wind maxima were observed on 24 out of 30 nights for which meteorological field experiments were conducted. Typical average windspeed profiles observed under the decoupled conditions showed windspeeds of the order of 1 to 2 m sec^{-1} near the surface, increasing to maximum values of 8 m sec^{-1} at 100 to 200 meters above the surface.

In summary, it appears that the nocturnal jet and nighttime flows are significant factors in the transport of pollutants over long distances.

Definitive studies on the long-range transport of atmospheric tracers have been primarily associated with radioactive debris (Islitzer and Slade, 1968) and in many instances at heights not of particular interest for air pollution-related work. Some analyses of ambient data have been performed to provide qualitative indications of the long-range transport and dispersion of certain pollutant species (Altshuller, 1976; Lyons and Husar, 1976; Rodhe et al., 1972; Brosset and Akerstrom, 1972); but very few quantitative studies exist, primarily because of a lack of appropriate experimental data. Recent monitoring and field studies of long-range air pollutant transport phenomena should alleviate this problem somewhat (Perhac, 1978; MacCracken, 1978; Schiermeier et al., 1979).

6.5 AIR QUALITY SIMULATION MODELING

The air quality simulation model (AQSM) primarily describes the quantitative relationship between the distribution of emissions and ambient air quality in time and space. Air quality simulation models are intended to improve understanding of the physical and chemical processes operating in polluted atmospheres and provide a basis for sound, credibly based scientific decisions on the nature and extent of emission control required to meet specified ambient air quality standards.

The AQSM was first developed in the early 1930's, when Sutton (1932) introduced his basic theory on diffusion in the atmosphere. Sutton's theory established the foundation for the Gaussian equations used in describing the dispersion of effluents in the atmosphere. Since then, the evolution of AQSM's has continued, treating increasingly complex air pollution problems and using advanced theoretical approaches to describe the details of physical and chemical atmospheric processes. The use of mathematical models for air quality impact analysis associated with SO_2 and total suspended particulate matter, both criteria pollutants, had become a standard practice, though discretionary, prior to the passage of the Clean Air Act Amendments in 1977.

With the passage of the 1977 amendments, EPA was required to take certain regulatory steps related to the use of air quality simulation models. The workhorse of operational air quality simulation modeling has been the single and multiple source Gaussian plume models. These models have been used primarily to predict ground-level concentrations ranging from the immediate vicinity to several kilometers downwind of the effluent source. Many reviews on dispersion modeling are available (e.g., Gifford, 1968; Strom, 1976; and Turner, 1979). Section 6.5.1 provides a brief discussion of the status of the Gaussian modeling techniques, while section 6.5.2 discusses the scientific basis and current status of air quality simulation modeling over long distances, and the extent to which available modeling techniques have furthered our understanding of the physical and chemical processes affecting the fate of SO_2 and particulate matter in the air environment. A discussion of model evaluation and data bases is provided in Section 6.5.3.

6.5.1 Gaussian Plume Modeling Techniques

The Gaussian diffusion formulation is used in a variety of air quality simulation modeling approaches. The formulation is a result of the Gaussian or normal distribution function being a fundamental solution to the Fickian diffusion equation. Strictly speaking, the Gaussian distribution applies only in the limit of large diffusion time and for homogeneous, stationary conditions.

The Gaussian diffusion formulation for a continuous point source emitting pollutants at height h and calculated receptor concentrations at ground level is given by

$$\chi\,(x,y) = \frac{Q}{\pi \sigma_y \sigma_z u} \exp\left[-\left(\frac{y^2}{2(\sigma_y)^2} + \frac{h^2}{2(\sigma_z)^2} \right)\right] \qquad (6\text{-}1)$$

where χ is the time-averaged ground-level concentration at horizontal coordinates (x,y); Q is the continuous source strength; u is the time-averaged magnitude of the wind velocity in the x direction (considered constant and unidirectional over the height interval between the source and the ground); and σ_y and σ_z are the standard deviations of the concentration distribution in the y and z directions. The horizontal dispersion coefficient, σ_y, and the vertical dispersion coefficient, σ_z, are functions of atmospheric stability and are empirically derived. The above formulation assumes perfect ground reflection by the pollutant species. The formula may be altered to include a reduction factor to consider surface absorption. Graphical and analytical expressions for σ_y and σ_z are available as a function of downwind distance from the source and atmospheric stability, based on experimental observation of smoke and pollutant releases (see, for example, Turner, 1970).

The Gaussian modeling approach has been applied to point, line, and area source emission configurations. When applied to multiple source problems, contributions from individual sources to a receptor concentration can be calculated separately and added to give the total contribution to the receptor region. The Gaussian technique has been used extensively because of its simplicity, low operational costs, ease of use, and general utility in air pollution applications.

The Gaussian plume model formulas, however, have not been without criticism. Aside from fundamental disadvantages, such as inability to treat spatially varying meteorological parameters, discontinuity under calm wind conditions, and inability to treat nonlinear reactive pollutants, the major criticisms relate to the improper application of the models through the use of inadequate or inappropriate input data. Turner (1979) pointed out that the ease of using the Pasquill-Gifford dispersion estimates rather than collecting recommended onsite meteorological data for developing inputs to the model has led to applications beyond the scope intended for the dispersion schemes. Turner (1979) indicates that a significant improvement in dispersion modeling estimates would be achieved through the collection and use of onsite measurements, including: hourly averaged windspeed and direction at a height of 10 m; standard deviation of horizontal wind fluctuations; bulk Richardson number (a quantitative measure of atmospheric stability) as determined from temperature and 2 and 10 m temperature differences; height of the top of the boundary layer under unstable conditions; and the top of the inversion under stable atmospheric conditions. Additional improvements will grow as existing theories and experimental data bases are drawn together in a unified scheme for estimating dispersion parameters as a function of stability, effluent release height, and surface roughness.

A variety of operational Gaussian air quality dispersion models, used for most SO_2 and total suspended particulate matter regulatory applications, are available through EPA's User's Network for Applied Modeling of Air Pollution (UNAMAP). Turner (1979) briefly describes these models.

A final aspect of dispersion modeling calculations is the prediction of the effective height of the effluent release, the so-called "plume rise," which strongly affects the predicted ground-level concentration of pollutants. Research into the processes affecting plume rise and its prediction has been underway for the past 20 years. Briggs (1975) reviewed the physics of plume rise and its prediction and presented basic formulations for calculating the height to which plumes rise as a function of atmospheric stability and several standard stack parameters. He indicated that further investigation is needed in the area of plume rise limited by ambient turbulence under convective atmospheric conditions.

6.5.2 Long-Range Air Pollution Modeling

The recent growing interest in long-range transport of air pollutants has resulted from extensive reviews on the subject by Bass (1980), Eliassen (1980), Pack et al. (1978), and Smith and Hunt (1978). (Long range is defined in this document as horizontal scales of the order of 1000 km resulting from transport times of the order of several days.) Typical model spatial resolutions on this scale range from 20 to 100 km. Bass (1980) concluded that most long-range transport models are Lagrangian based. In the Lagrangian approach, an emitting source element is represented by a series of discrete pollutant parcels that are advected and diffused by a time- and space-dependent wind field. In principle, calculation on the individual pollutant parcels can treat time-dependent chemical transformation, dry deposition, and precipitation scavenging processes. Fixed space-time averages of pollutants are generated by superimposing all elements that pass a specified point over the averaging time of interest. The Lagrangian models, although all based on the same theory, have evolved individual nuances.

Little consensus of opinion exists for standard treatments of: (1) wind field analysis; (2) choice of wind height level for trajectory; (3) mixing height variations; and (4) dry and wet removal and chemical transformation rates. Even the basic generation of discrete air parcels is viewed from four different approaches: puff superposition, segmented plume, square puff, and statistical. In Figure 6-7, three of the approaches are contrasted to the idealized continuous plume they are attempting to represent (Bass, 1980).

Eulerian or grid-based approaches are less prevalent in long-range transport air pollution modeling. This may result from problems associated with the numerical integration of the advection equation that give rise to pseudodiffusion effects. A more likely reason is the increased complexity and enhanced data base and computation requirements of the Eulerian models.

Table 6-7 provides a representative sampling of long-range transport models discussed in the available literature and for each referenced model, presents a brief description of the modeling approach, including characteristic averaging times; approaches to dry and wet removal and chemical transformation; and pollutant species modeled.

A review of the models presented in Table 6-7 indicates that SO_2 and sulfates have received the most attention. This is because many of the models were developed specifically to study the acid rain phenomenon. These sulfur species have been identified as major contributors to the acidification of precipitation. Though none of the models consider primary emitted particulate matter, its inclusion would be reasonably straightforward given the availability of appropriate emission inventories. Considering the gas-to-particle forming processes of nitrates and organic species, aerosol dynamic processes and size distributions need further research to be understood. Until these basic processes, as well as gas-liquid phase transfer and solution phase chemistry of rain droplets, are treated adequately within the models, significant skepticism toward the scientific credability and usefulness of the models will remain.

Similarly, regional visibility impairment, which results from the physical interaction of sunlight with light-absorbing gases and particles, and light-scattering aerosols, requires the consideration of many of the processes described above. Though several empirical analysis techniques have been developed that provide a qualitative understanding of the scope and general meteorological characteristics of the visibility impairment problem, no adequate quantitative relationships are available for emission control strategy assessments.

Although verification studies of long-range transport models are limited, it has been recognized for some time that errors in observed wind direction (Pack et al. 1978) and the specification of wind fields in general (Sykes and Hatton, 1976; Smith and Hunt, 1978; Draxler, 1979) can result in drastic errors in spatial predictions over long-range travel distances.

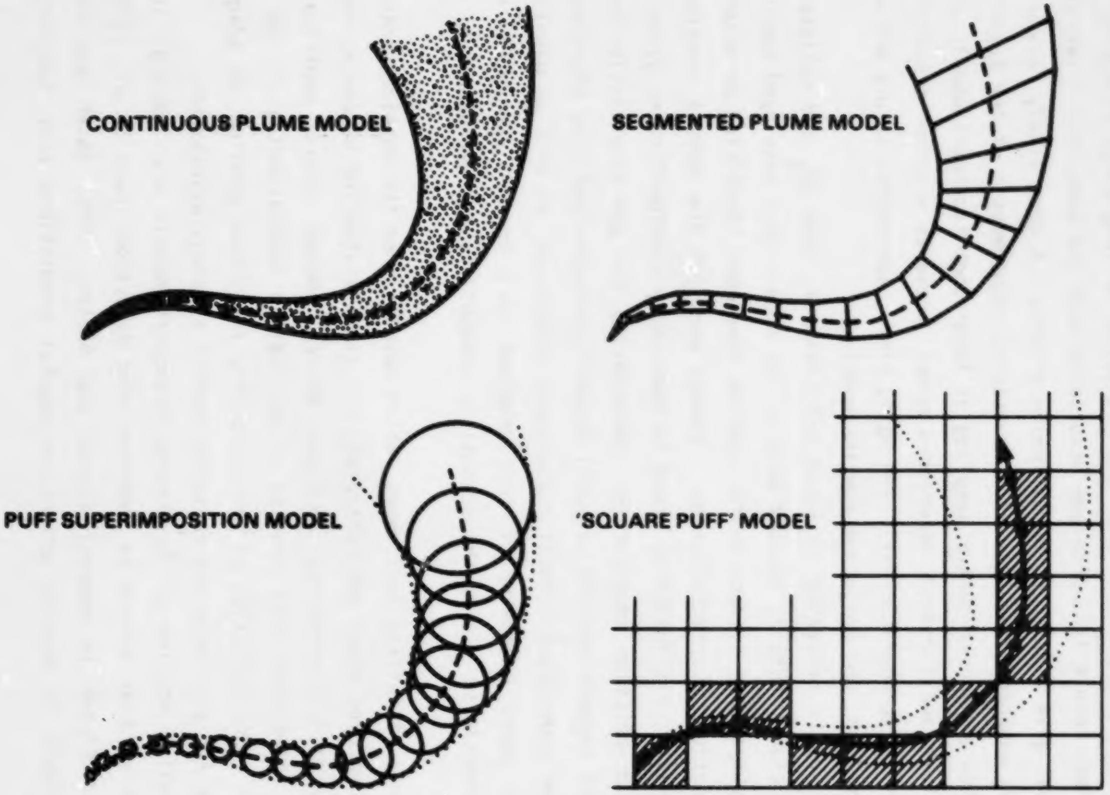
CONTINUOUS PLUME MODEL
SEGMENTED PLUME MODEL
PUFF SUPERIMPOSITION MODEL
'SQUARE PUFF' MODEL

Figure 6-7. Trajectory modeling approaches are shown.
Source: Bass (1980).

TABLE 6-7. SUMMARY OF SELECT LONG RANGE TRANSPORT AIR POLLUTION MODELS

Model	Type	Description averaging time	Removal process	Chemical process	Pollutant species	Reference
ARL-ATAD[1]	Segmented plume trajectory	daily to yearly	First order wet and dry removal	None	Inert substances	Heffter et al. (1975) Heffter (1980)
EURMAP-1,-2[2] ENAMAP-1	Puff superimposition trajectory	daily to yearly	First order wet and dry removal	SO_2 first order decay	SO_2 and SO_4^{2-}	Johnson et al. (1978) Mancuso et al. (1979) Bhumralkar (1980)
MESOPUFF[3]	Puff superimposition trajectory	daily to yearly	First order dry removal	SO_2 first order decay	SO_2 and SO_4^{2-}	Benkley and Bass (1979a)
MESOPLUME[4]	Segmented plume trajectory	daily to yearly	First order dry removal	SO_2 first order decay	SO_2 and SO_4^{2-}	Benkley and Bass (1979b)
ASTRAP[5]	Statistical trajectory	monthly to yearly	Diurnal and seasonal dry removal/ first order wet removal	Diurnal and seasonal dependent SO_2 first order decay	SO_2 and SO_4^{2-}	Shannon (1979) Shieh (1977)
AIRSOX	Puff superimposition trajectory/vertical finite difference	daily to yearly	First order wet and dry removal	SO_2 first order decay	SO_2 and SO_4^{2-}	Meyers et al. (1979)
MESOGRID[6]	Squence puff grid	daily to monthly	First order wet and dry removal	Typically SO_2 first order decay	SO_2 and SO_4^{2-}	Morris et al. (1979)

[1] see also model by Start and Wendell (1974)

[2] see also models by Eliassen (1978), Nordo (1976) and Eliassen and Saltbones (1975)

[3] see also models by Draxler (1977, 1979)

[4] see also models by McNaughton (1980); Hales et al. (1977); Pendergast (1979); and Henmi (1980)

[5] see also models by Bolin and Persson (1975); Fisher (1975, 1978); and and Scriven and Fisher (1975)

[6] see also models by Lui and Durran (1977); Rao et al. (1976); Lavery et al. (1980); and Carmichael and Peters (1979)

The sparse temporal and spatial resolution of upper-level wind information leads to uncertainties in predicting transport residues. The National Weather Service's rawinsonde network provides vertical profiles for windspeed and direction, temperature, and moisture every 12 hours at 70 sites across the continental United States. This provides upper-level winds at a horizontal resolution of the order of 400 kilometers, considerably less resolved than the 20 to 80 kilometer grid spacing required in air quality simulation modeling techniques. Increased temporal resolution in upper-level winds should also diminish transport prediction uncertainties.

6.5.3 Model Evaluation and Data Bases

Almost no long-range transport models have been verified through comparison of model predictions with actual observation. The major deterrent has been insufficient or inappropriate monitoring data for the spatial scales of interest. Long-range transport models predict ambient pollutant concentrations that represent horizontal spatial averages of the order of 10^3 square kilometers. Standard monitoring networks, established for local high concentration measurement within the vicinity of the emission sources, do not provide representative data for long-range models. Some routine monitoring data for SO_2 and SO_4^{2-} from EPA's Storage and Retrieval of Aerometric Data (SAROAD) system have been useful in model testing (Bhumralkar, 1980) but in general, the data have proven less than adequate. The Electric Power Research Institute (EPRI)-sponsored Sulfate Regional Experiment (SURE) air quality network, (Perhac, 1978) which operated from August 1977 to October 1978, has provided the most extensive SO_2 and SO_4^{2-} data base to date for long-range transport model evaluation. But even these data collected over this limited period are only sufficient in providing spatially resolved SO_2 and SO_4^{2-} regional concentration fields during the intensive study periods--August 1977, October 1977, mid-January to mid-February 1978, April 1978, July 1978, and October 1978--when the extended 54-site monitoring network was activated. During the SURE study period, data also exist from the Department of Energy-funded Multi-State Atmospheric Power Production Pollution Study (MAP3S) precipitation chemistry network, (MacCracken, 1978) which had at least four sites operating during the program. No dry deposition data are available for the study period. Since the data have only recently become available, they have had limited use, but future long-range transport model evaluations are certain to consider them.

Another limitation in model evaluation studies is the quality of the emission inventory. Until recently, there was no national gridded emission inventory. Clark (1980) prepared an annual gridded emissions inventory for the United States and Southern Canada east of the Rocky Mountains, using data compiled by EPA, the Ontario Ministry of the Environment, and Environment Canada. In preparing the gridded inventory, Clark found significant errors in many of the United States point source records, which had to be corrected. Models, like chains, are only as strong as their weakest links.

Although long-range transport model evaluations are extremely limited, two recent studies should be noted. Mancuso et al. (1979) evaluated a trajectory puff model using monthly averages from the Organisation for Economic Cooperation and Development (OECD) monitoring program. They generated two sets of evaluation results. The first considered model predictions versus observations using parameters originally specified for the model. This resulted in root mean square (RMS) differences of predicted versus observed monthly averaged concentration at all receptors of 12.9 (5 ppb) and 4.8 μg/m^3 for SO_2 and SO_4^{2-}, respectively. In the second evaluation, half of the data were used to optimize model parameters through a regression analysis technique and the other half of the data were used to evaluate the model. This resulted in RMS differences of 7.7 (3 ppb) and 2.9 μg/m^3 for SO_2 and SO_4^{2-} and correlation coefficients of 0.72 both for SO_2 and SO_4^{2-}, a marked improvement in the model's performance. None of the optimized parameters assumed values that were physically unrealistic. Lavery et al. (1980) evaluated a grid model using data from the SURE monitoring network and based on 24-hour averaged concentrations. Four days were selected for parameter "adjustments" and "fine tuning" and an additional three days were used for the model evaluation. RMS differences for SO_4^{2-} ranged from 6.9 to 23.4 μg/m^3 for the 3 days, with a mean value of 14.1 μg/m^3. RMS differences for SO_4^{2-} ranged from 5.2 to 14.4 μg/m^3 with a mean value of 9.3 μg/m^3. Mean concentration for the 3 days were 26.1 (10 ppb) and 13.9 μg/m^3 for SO_2 and SO_4^{2-}, respectively. Mean correlation coefficients for SO_2 and SO_4^{2-} for the three days tested were 0.31 and 0.53, respectively. Based on results of the 3-day comparison between observations and model predictions, Lavery et al. (1980) concluded that the model typically overpredicts observed 24-hour average sulfate by 20 to 30 percent and observed 24-hour average SO_2 by a factor of 2 to 3.

Overall, the results from both models are encouraging. Evaluation of a trajectory puff model for the United States (Bhumralkar, 1980) using the SURE data base, is also showing promising results.

6.5.4 Atmospheric Budgets

Atmospheric budgets have proven a convenient technique for quantitatively evaluating the overall source and sink contributions of specified pollutant species within a selected region of interest. The budget is formed by estimating the various input and output processes associated with the region, such as anthropogenic and natural emissions, pollutant concentration inflow and outflow, and wet and dry removal. Budget analyses provide a general long-term indication of the significant factors contributing to the pollutant burden in a given region. Sulfur budgets have been of interest both in Europe (Rodhe, 1972, 1978; Garland, 1978) and in North America (Galloway and Whelpdale, 1980) because of the association of sulfur with acid precipitation phenomena. Conclusions drawn from the eastern North American sulfur budget by Galloway and Whelpdale (1980) were that manmade emissions exceed natural ones by a factor of 10; wet and dry deposition over the region is approximately equivalent; and at least one-quarter of the emissions leave the region via the atmosphere to the east. As with Western Europe, the North American budget showed that human activities dominate the regional atmospheric sulfur cycle.

6.6 SUMMARY

The processes governing transport and diffusion, chemical transformation, and wet and dry removal of SO_2 and PM in the atmosphere are extremely complex and are not completely understood. The oxidation rates of SO_2 observed in industrial plumes and urban atmospheres range from 0 to 15 percent/h and would seem to be only partially accounted for through homogeneous gas-phase reactions. Liquid-phase catalytic oxidation reactions involving Mn^{2+} and carbon, as well as solution-phase oxidation by H_2O_2 are possible contributors to the observed oxidation rates, but further research is required to determine the rates and detailed mechanisms of these processes under typical atmospheric conditions.

Dry deposition of SO_2 is fairly well understood as a result of extensive measurements over various surfaces. Particle dry deposition studies have focused more on the physical aspects of the deposition process, and have generated very few supporting data on particles with compositions typical of those found in the polluted atmosphere.

Our understanding of the wet removal of SO_2 has progressed considerably in recent years, including consideration of solution-phase chemistry within rain droplets. Particle removal, like gas removal, depends on the physical characteristics of the precipitation events, which may, in many instances, be the determining factors in accurate wet removal prediction.

Characterization of the dynamics of the planetary boundary layer is essential to an adequate understanding of pollutant transport and diffusion over all spatial scales. Though considerable advances have been made in this area, our ability to predict mean transport and diffusion over long distances is inadequate. No doubt this is partly due to the sparse spatial and temporal resolution of the data from the upper air wind observation network used to generate models of the transport winds.

Present generation long-range air pollutant transport models use simple parameterization for chemical transformation and wet and dry removal, and varying degrees of sophistication in the treatment of transport and diffusion. None of the models adequately treat the dynamics of the planetary boundary layer. Evaluations of long-range transport models, though limited because of lack of data bases, have shown that with further research and development these models should be adequate tools in addressing air pollution issues associated with the mean movement of pollutants over long distances.

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7. ACIDIC DEPOSITION

7.1 INTRODUCTION

Acidic precipitation has become a major environmental concern in many regions of the world. Acidic precipitation (rain and snow) in the Adirondack Mountains of New York State, eastern Precambrian Shield area of Canada, southern Norway, and southwest Sweden has been associated with the acidification of waters in ponds, lakes, and streams and the subsequent disappearance of animal and plant life. Acidic precipitation also is believed to have the potential for leaching elements from sensitive soils and causing direct and indirect injury to forests. It is also believed to play a role in damaging stone monuments and buildings, corroding metals and the deterioration of paint.

The story of acidic precipitation is ever-changing; new information concerning the phenomenon is appearing continuously. This chapter explains how particulate matter and sulfur oxides are involved in acidic deposition phenomena and associated ecological effects. The information as presented reflects the understanding of the scientific community at the time this chapter was written. A critical assessment document on acidic decomposition currently being written under the direction of the Office of Research and Development of the Environmental Protection Agency, will present a more detailed, up-to-date discussion of the many facets of the acidic deposition problem.

The sections that follow emphasize the effects associated with the wet deposition of sulfur and nitrogen oxides and their products on aquatic and terrestrial ecosystems. Dry deposition also plays an important role, but the relative contribution of this process is still unknown. Because sulfur and nitrogen oxides are so closely linked in the formation of acidic precipitation, no attempt has been made to limit the discussion that follows to sulfur oxides.

7.1.1 Overview of the Problem

The generally held hypothesis is that sulfur and nitrogen compounds are largely responsible for the acidity of precipitation. The emissions of the sulfur and nitrogen compounds involved in acidification are attributed chiefly to the combustion of fossil fuels. Emissions may occur at ground level, as from automobile exhausts, or from stacks 300 meters (1000 feet) or more in height. Emissions from natural sources are also involved; however, in highly industrialized areas, emissions from manmade sources far exceed those from natural sources. In the eastern United States, the highest emissions of sulfur oxides are from electric power generators burning coal, while on the West Coast, particularly around large cities, emissions of nitrogen oxides, chiefly from automotive sources, predominate. (See Chapter 4.)

The fate of sulfur and nitrogen oxides, as well as other pollutants and gases emitted from natural sources into the atmosphere, depends on their dispersion, transport, transformation and deposition. Sulfur and nitrogen oxides may be deposited locally or transported long distances from the emission sources. Therefore, residence time in the atmosphere will be brief if the emissions are deposited locally or may extend to days or weeks if long range transport occurs. The chemical form in which emissions ultimately reach the receptor is determined by the complex chemical transformations that take place between the emission sources and the receptor. Long range transport over distances of hundreds or thousands of miles allows time for a greater number of chemical transformations to occur (see Chapter 6).

Sulfates and nitrates are among the products of the chemical transformations of sulfur and nitrogen oxides. Ozone and other photochemical oxidants are believed to be involved in the chemical processes that transform sulfur dioxide and nitrogen oxides in the atmosphere into sulfuric and nitric acids. When these acids are brought to earth in rain and snow, acidic precipitation occurs. Because of long range transport, acidic precipitation in a particular state or region can be the result of emissions from sources in states or regions many miles away, rather than from local sources. To date, however, the complex nature of the chemical transformation processes has made it difficult to demonstrate a direct cause and effect relationship between emissions of sulfur and nitrogen oxides and the acidity of precipitation.

Acidic precipitation is arbitrarily defined as precipitation with a pH less than 5.6. This value has been selected because precipitation formed in an atmosphere relatively free of natural or manmade emissions would have a pH of approximately 5.6 due to the combining of carbon dioxide with water in the air to form carbonic acid.

Acidity of aqueous solutions is determined by the concentration of hydrogen ions (H^+) present and is expressed in terms of pH units--the logarithm of the inverse activity of hydrogen ions. The pH scale ranges from 0 to 14, with a value of 7 representing a neutral solution. Solutions with values less than 7 are acidic, while values greater than 7 are basic. Because pH is a logarithmic scale, a change of one unit represents a tenfold change in acidity, hence pH 3 is ten times as acidic as pH 4. Currently the acidity of precipitation in the Northeastern United States normally ranges from pH 3.9 to 5.0; in other regions of the United States precipitation episodes with a pH as low as 3.0 have been reported. For comparison, the pH of some familiar substances are: cow's milk, 6.6; tomato juice, 4.3; cola (soft drink) 2.8; and lemon juice, 2.3.

The pH of precipitation can vary during an event, from event to event, from season to season, and from geographical area to geographical area. Substances in the atmosphere can cause the pH to shift by making it more acidic or more basic. Dust and debris swept up in small amounts from the ground into the atmosphere may become components of precipitation. In the West and Midwest soil particles tend to be basic, but in the eastern United States they tend to be acidic. Industrial emissions of limestone particles and similar oxides and carbonates are basic. As gaseous ammonia from decaying organic matter makes precipitation more basic, ammonia influences the acidity of precipitation in areas where there are large stockyards or other sources of organic matter.

In the Eastern United States sulfur oxide emissions are greater than nitrogen oxide emissions; hence, sulfates are greater contributors in this region to the formation of acids in precipitation. The ratio between the two emissions, however, has been decreasing. Sulfate concentrations are greater in summer than in winter in the Eastern United States; however, around some of the larger cities in California nitrates contribute more to the formation of acidity in rainfall. In coastal areas sea spray strongly influences precipitation chemistry by contributing sodium, calcium, potassium, chloride, and sulfates. In the final analysis, the pH of precipitation reflects the overall contributions of all of these components.

The impact of acidic precipitation on lakes, streams, ponds, forests, fields and manmade objects, therefore, is not the result of one, or even of several precipitation events, but of continued additions of acids or acidifying substances over time. When did precipitation become acidic? Some scientists state that it began with the Industrial Revolution and the burning of large amounts of coal; others say that, in the United States, it began with the introduction of tall stacks on power plants in the 1950's; other scientists disagree completely and state that rain has always been acidic. In other words, no definitive answer to the question exists at the present time, nor are there data to indicate with much confidence trends of pH in precipitation because the pH of rain has not been continuously monitored in the United States for any period of time. In Scandinavia, on the other hand, the pH of rain has been continuously monitored for many years; it is more nearly possible, therefore, to determine when precipitation began to become more acidic. Data from the European Chemistry Network in the late 1950's revealed that the pH of the precipitation falling on southwestern Scandinavia was < 4.7. At that time it was postulated that the acidification of freshwater lakes and streams which had first been noted in southern Norway in 1911 and later during the 1920's had been caused by acidic precipitation.

Though acidic precipitation (wet deposition) is usually emphasized, it is not the only process by which acids or acidifying substances are added to bodies of water or to the land. Dry deposition also occurs. During wet deposition, substances such as sulfur and nitrogen oxides are scavenged by precipitation (rain and snow) and deposited on the surface of the earth. Dry deposition processes include gravitational sedimentation of particles, impaction of aerosols, adsorption and absorption of gases by objects at the earth's surface or by the soil or water. Gases, solid and liquid aerosols can be removed by both wet and dry deposition. Dew, fog, and frost are also involved in the deposition processes but do not strictly fall into the category of either wet or dry deposition. Dry deposition processes are not as well understood as wet deposition at the present time; however, all of the deposition processes contribute to the gradual accumulation of acidic or acidifying substances in the environment. In any event, precipitation in the Eastern United States at the present time is acidic and has been associated with changes in ponds, lakes, and streams that are considered by humans to be detrimental to their welfare.

The most visible changes associated with both wet and dry acidic deposition are those observed in the lakes and streams of the Adirondack Mountains in New York State, the Precambrian Shield areas of Canada and in the Scandinavian countries. In these regions, the pH of the fresh water bodies has decreased, causing changes in animal and plant populations. The most readily observable effect, however, has been the decrease in fish populations.

The chemistry of fresh waters is determined primarily by the geological structure (soil system and bedrock) of the lake or stream catchment basin, by the ground cover and by land use. Near coastal areas, that is up to about 160 kilometers (100 miles) from the sea, marine salts also may be important in determining the chemical composition of the stream, river, or lake.

Sensitivity of a lake to acidification depends on the acidity of both wet and dry deposition plus the same factors--the soil system of the drainage basin, the canopy effects of the ground cover, and the composition of the watershed bedrock--that determine the chemical composition of fresh water bodies. The capability of a lake and its drainage basin to neutralize incoming acidic substances, however, is determined largely by the composition of the bedrocks.

Soft water lakes, those most sensitive to additions of acidic substances, are usually found in areas with igneous bedrock which contributes few soluble solids to the surface waters, whereas hard waters contain large concentrations of alkaline earths (chiefly bicarbonates of calcium and sometimes magnesium and iron) derived from limestones and calcareous sandstones in the drainage basin. Alkalinity is associated with the capacity of lakes to neutralize or buffer the incoming acids. The quantity of acidic precipitation necessary to acidify a sensitive lake system has yet to be determined.

The disappearance of fish populations from freshwater lakes and streams is usually one of the most readily observable signs of lake acidification. Death of fish in acidified waters has been attributed to the modification of a number of physiological processes by a change in pH. Two patterns of pH change have been observed; the first involves a sudden short-term drop in pH and the second, a gradual decrease in pH with time. Sudden short-term drops in pH often result from a winter thaw or the melting of the snow pack in early spring and the release of the acidic constituents of the snow into the water. These short-term changes in water chemistry may have significant impacts on aquatic biota, especially if they occur at sensitive times in the life cycle (e.g., during spawning or early stages of development).

A gradual decrease in pH, particularly below 5, can interfere with reproduction and spawning of fish until elimination of the population occurs. In some lakes, aluminum mobilization in fresh waters at a pH below 5 has resulted in fish mortality .

Although the disappearance of and/or reductions in fish populations are usually emphasized as significant results of lake and stream acidification, changes of equal or greater importance are the effects on other aquatic organisms ranging from waterfowl to bacteria. Organisms at all trophic (feeding) levels in the food web appear to be affected. Reduction in number and diversity of species may occur; biomass (total mass of living organisms in a given volume of water) may be altered and processes, such as primary production and decomposition, impaired.

Primary production and decomposition are the bases of the two major food webs (grazing and detrital) within an ecosystem by which energy is passed along from one organism to another through a series of steps of eating and being eaten. Green plants, through the process of photosynthesis, are the primary energy producers in the grazing web, while bacteria initiate the detrital food web by feeding on dead organic matter. Disruption of either of these two food webs results in a decrease in the supply of nutrients, interferes with their cycling, and also reduces energy flow within the affected ecosystems. Acidification of lakes and streams affects both these processes when a slowing down in the rate of microbial decomposition causes an alteration of the species composition and structure of the pondweed and algae plant communities.

At present, there are no documented observations or measurements of changes in natural terrestrial ecosystems that can be directly attributed to acidic precipitation. The information available is an accumulation of the results of a wide variety of controlled research approaches largely in the laboratory, using in most instances some form of "simulated" acidic rain, frequently dilute sulfuric acid.

Soils may become gradually acidified from an influx of hydrogen (H^+) ions. Leaching of the mobilizable forms of mineral nutrients may occur. The rate of leaching is determined by the buffering capacity of the soil as well as the amount and composition of precipitation. Unless the buffering capacity of the soil is high and/or the salt content of precipitation is high, leaching will, in time, result in acidification. At present, there are no studies showing this process has occurred because of acidic precipitation.

Damage to stone monuments and buildings, corrosion of metals and deterioration of paint can result from acidic precipitation. Because sulfur compounds are a dominant component of acidic precipitation and are deposited during dry deposition also, the effects resulting from the two processes cannot be distinguished. In addition, the deposition of sulfur compounds on stone surfaces provides a medium for microbial growth that can result in deterioration. (See Chapter 10 for a more detailed discussion of materials effects.)

Human health effects due to the acidification of lakes and rivers have been postulated. Fish in acidified water may contain toxic metals mobilized due to the acidity of the water. Drinking water may contain toxic metals or leach lead from the pipes bringing water into the homes. Humans eating contaminated fish or drinking contaminated water could become ill. No instances of these effects having occurred have been documented.

Several aspects of the acidic precipitation problem remain subject to debate because existing data are ambiguous or inadequate. Important unresolved issues include:

1. The rate at which rainfall is becoming more acidic and the rate at which the phenomenon is becoming geographically widespread.

2. The relative extent to which the acidity of rainfall in a region depends on local emissions of nitrogen and sulfur oxides versus emissions transported from distant sources.
3. The relative importance of changes in total mass emission rates compared to changes in the nature of the emission patterns e.g., ground level versus tall stacks in contributing to regional acidification of precipitation.
4. The relative contribution of wet and dry deposition to the acidification of lakes and streams.
5. The geographic distribution of natural sources of NO_x and SO_x, and NH_3 and the significance and seasonality of their contributions.
6. The existence and significance of anthropogenic, non-combustion sources of SO_x, NO_x and HCl.
7. The dry deposition rates for SO_2, NO_2, sulfate, nitrate and HCl over various terrains and seasons of the year.
8. The existence and reliability of long-term pH measurements of lakes and headwater streams.
9. The acceptability of current models for predicting long range transport of SO_x and NO_x and of those for predicting the acid tolerance of lakes.
10. The feasibility and costs of using liming or other corrective procedures to prevent or reverse damage from acidification.
11. The differential effects of SO_x and NO_x and hydrogen ion deposition on ecosystem dynamics in both aquatic and terrestrial ecosystems.
12. The effectiveness of fertilization resulting from sulfate and nitrate deposition on soils.
13. The ultimate effects of acidic deposition on agricultural crops, forests, and other native plants.
14. The effects of acidic deposition on soil microbial processes and nutrient cycling.

7.1.2 Ecosystem Dynamics

In the natural world there is no action without a reaction. An extremely close mutual relationship exists between the chemistries of the environment and of living organisms. There is a continuing exchange of nutrients and energy. The flow of the two are closely intertwined and involve processes that have been in existence for millions of years. Any action that changes the rate or amount of nutrient and/or energy flow will cause a change in the relation ships that exist between the environment and living organisms: ecosystem dynamics involves the response and adaptation of biological communities to the changing environment.

Life on Earth depends on the movement of energy and minerals through the biosphere, that thin layer of life surrounding the earth. The living systems (forest, grasslands, cultivated fields, lakes, rivers, estuaries, and oceans) within the biosphere obtain energy from the sun, nutrients from the earth's crust (the lithosphere), gases from the atmosphere, and water from the hydrosphere. All of the living systems are interdependent. Energy and nutrients move from one to another. The living systems, together with their physical environments, the lithosphere, hydrosphere and atmosphere make up the ecosystem that is the planet Earth (Billings, 1978; Boughey, 1971; Odum, 1971; Smith, 1980).

Ecosystems are composed of biotic (living) and abiotic (nonliving) components. The biotic component consists of: (1) producers, green plants that capture the energy of the sun; (2) consumers that utilize as their energy source the food stored by the producers; and (3) decomposers who obtain their energy by breaking down and converting dead organic matter into inorganic compounds. (See Table 7-1). The abiotic components are air, water, the soil matrix, sediment, particulate matter, dissolved organic matter, and nutrients in aquatic systems, and dead or inactive organic matter in terrestrial systems (see Table 7-1) (Billings, 1978; Boughey, 1971; Smith, 1980).

Ecosystems are basically energy processing systems "whose components have evolved together over a long period of time. The boundaries of the system are determined by the environment, that is, by what forms of life can be sustained by the environmental conditions of a particular region. Plant and animal populations within the system represent the objects through which the system functions." (Smith, 1980).

Ecosystems are open systems. They both receive from and contribute to the environment that surrounds them. The environment contributes gases, nutrients, and energy. Ecosystems utilize these substances and, in turn, make their own contributions to the environment. Energy flows through the system unidirectionally while water, gases and nutrients are usually recycled and fed back into the system. The functioning of ecosystems is greatly influenced by the extent to which the gases and nutrients are fed back into the system. When materials are not returned to an ecosystem through recycling, they must be obtained in another way. The organismal populations are the structural elements of the ecosystem through which energy flows and nutrients are cycled. (Smith, 1980; Billings, 1978; Odum, 1971).

Energy from the sun is the driving force in most ecosystems. Without it, virtually all ecosystems would cease to function. The energy of the sun is captured by green plants through the process of photosynthesis and is stored in plant tissues. This stored energy is passed along through ecosystems by a series of feeding steps, known as food chains, in which organisms eat and are eaten. Energy flows through ecosystems in two major food chains, the grazing food chain and the detrital food chain. The amount of energy that passes through the two food chains varies from community to community. The detrital food chain is dominant in most terrestrial and shallow-water ecosystems. The grazing food chain may be dominant in deep-water aquatic ecosystems (Smith, 1980). The two fundamental processes involved in these two food chains are: (1) photosynthesis, the capture of energy from the sun by green plants, and (2) decomposition, the final dissipation of energy and the reduction of organic matter into inorganic nutrients.

TABLE 7-1. COMPOSITION OF ECOSYSTEMS

Component	Description
Biotic (biological):	
Individuals	Plants, animals (man), and microorganisms. These are either producers, consumers, or decomposers.
Producers	Green plants.
Consumers	Herbivores, carnivores.
Decomposers	Macroorganisms (mites, earthworms, millipedes, and slugs) and microorganisms (bacteria and fungi).
Populations	Groups of interbreeding organisms of the same kind, producers, consumers or decomposers, occupying a particular habitat.
Communities	Interacting populations linked together by their responses to a common environment.
Abiotic (physical):	
Atmosphere	Cosmic radiation, temperature, thermal radiation, radioactivity including fallout.
	Water vapor, cloud and precipitation.
	Gases, pressure and wind, Heat and temperature, Fire and pollutants
Lithosphere	Rock and soil particles
	Minerals, water, Radioactivity, heat and temperature, gases Topography
Earth mass	Gravity

Adapted from Billings (1978).

In addition to the flow of energy, the existence of the living world depends upon the circulation of nutrients through the ecosystems. Both energy and nutrients move through the ecosystem as organic matter. It is not possible to separate one from the other. Both influence the abundance of organisms, metabolic rate at which they live, and the complexity and structure of the ecosystem (Smith, 1980). Nutrients, unlike energy, after moving from the living to the nonliving return to the living components of the ecosystem in a perpetual cycle. It is through the cycling of nutrients that plants and animals obtain the minerals necessary for their existence.

The gaseous and sedimentary cycles are the two basic types of nutrient or biogeochemical cycles. The gaseous cycles involve carbon, oxygen, and nitrogen. Water, also, is sometimes considered as belonging to the gaseous cycle. In the gaseous cycles, the main nutrient reservoir is the atmosphere and the ocean. In the sedimentary cycle, to which phosphorus belongs, the reservoir is the soil and rocks of the earth's crust. The sulfur cycle, a combination of the two cycles, has reservoirs in both the atmosphere and earth's crust.

Nitrogen, sulfur and water cycles are involved in acidic deposition. Nitrogen, through the agency of plants (chiefly legumes and blue green algae) and microorganisms, moves from the atmosphere to the soil and back (see Figure 7-1). Human intrusion into the nitrogen cycle includes the addition of nitrogen oxides to the atmosphere, and ammonia and nitrates to aquatic ecosystems. Sulfur enters the atmosphere from volcanic eruptions, weathering, the surface of the ocean, gases released in the decomposition processes, and combustion of fossil fuels (see Chapter 4 for details). There is no way to harness or use energy without creating an environmental impact. Both the nitrogen and sulfur cycles have been overloaded in some parts of the world by the combustion of fossil fuels by man. For these cycles to function, an ecosystem must possess a number of structured relationships among its components. By changing the amounts of nitrogen and sulfur moving through the cycles, humans have perturbed or upset the structured relationships that have existed for millions of years and altered the movement of the elements through the ecosystems. The pathways that the elements take through the system depend upon the interaction of the populations and their relationships to each other.

Change is one of the basic characteristics of our environment. Weather changes from day to day, temperatures rise and fall, rains come and go, soils erode, volcanoes erupt, and winds blow across the land. These are natural phenomena. Significant environmental changes also result when human beings clear forests, build cities and factories, and dam rivers. All of these environmental changes influence the organisms that live in the ecosystems where the changes are occurring (Moran et al., 1980).

Existing studies indicate that changes occurring within ecosystems, in response to pollution or other disturbances, follow definite patterns that are similar even in different ecosystems. It is possible, therefore, to predict the basic biotic responses of an ecosystem to disturbances caused by environmental stress (Woodwell, 1970; Woodwell, 1962; Odum, 1965). These responses to disturbance are: (1) removal of sensitive organisms at the species and

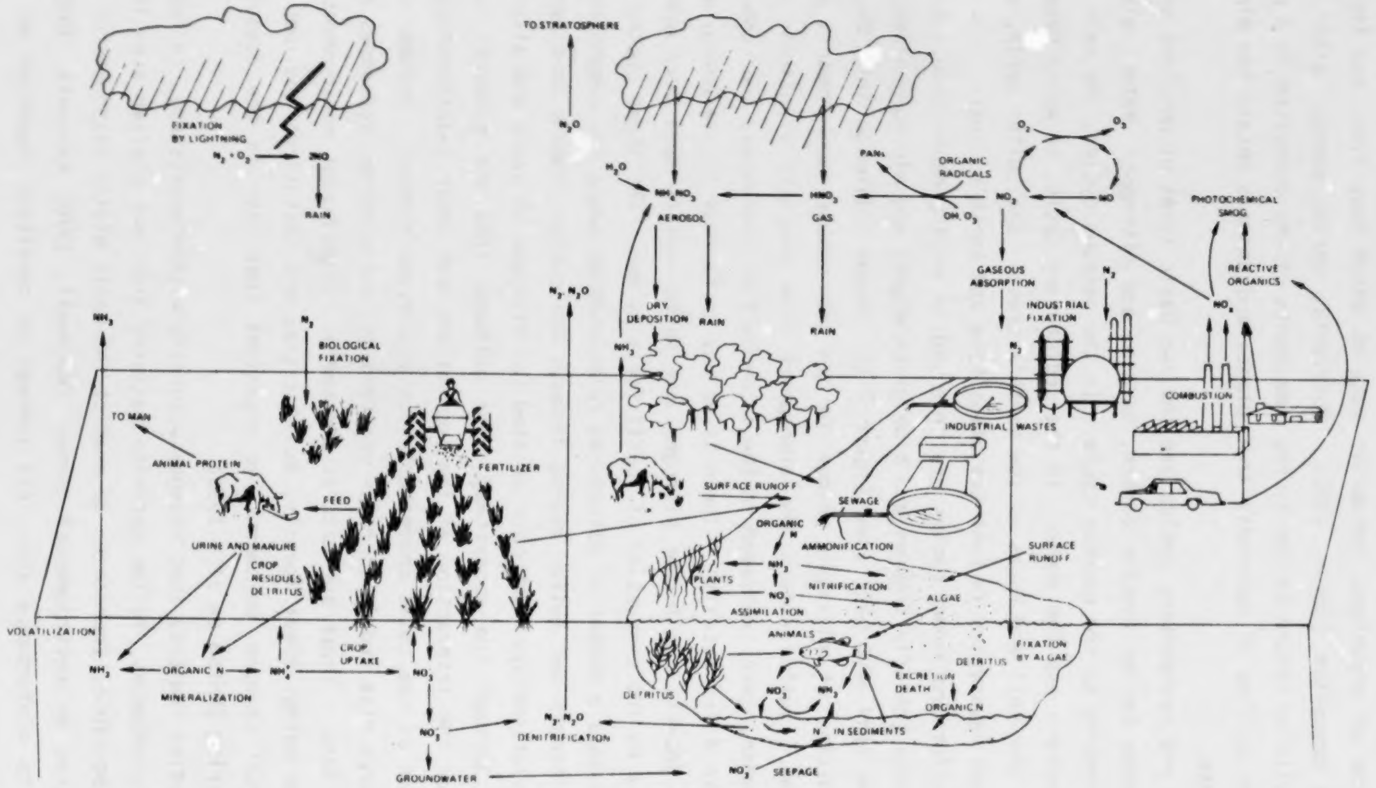

TO STRATOSPHERE
FIXATION BY LIGHTNING
$N_2 + O_2$
2NO
RAIN
N_2O
H_2O
NH_4NO_3
AEROSOL
HNO_3
GAS
PAN
ORGANIC RADICALS
OH, O_3
NO_2
O_2
O_3
NO
PHOTOCHEMICAL SMOG
REACTIVE ORGANICS
NO_x
GASEOUS ABSORPTION
N_2
INDUSTRIAL FIXATION
COMBUSTION
INDUSTRIAL WASTES
DRY DEPOSITION
RAIN
RAIN
N_2, N_2O
NH_3
N_2
BIOLOGICAL FIXATION
NH_3
TO MAN
ANIMAL PROTEIN
FEED
FERTILIZER
URINE AND MANURE
CROP RESIDUES DETRITUS
SURFACE RUNOFF
SEWAGE
ORGANIC N
AMMONIFICATION
NH_3
PLANTS
NO_3
NITRIFICATION
ASSIMILATION
ALGAE
SURFACE RUNOFF
VOLATILIZATION
NH_3
ORGANIC N
NH_4^+
MINERALIZATION
CROP UPTAKE
NO_3
NO_3^-
N_2, N_2O
DENITRIFICATION
ANIMALS
DETRITUS
NO_3^-
NH_3
EXCRETION DEATH
DETRITUS
FIXATION BY ALGAE
ORGANIC N
N IN SEDIMENTS
GROUNDWATER
NO_3^-
SEEPAGE

Figure 7-1. Schematic representation of the nitrogen cycle, emphasizing human activities that affect fluxes of nitrogen (National Research Council, 1978).

subspecies level due to differential kill; (2) reduction in the number of plants and animals (standing crop); (3) inhibition of growth or reduction in productivity; (4) disruption of food chains; (5) return to a previous state of development; and (6) modification in the rates of nutrient cycling.

Ecosystems can respond to environmental changes or perturbations only through the response of the populations of organisms of which they are composed (Smith, 1980). The species of organisms sensitive to environmental changes are removed. Therefore, the capacity of an ecosystem to maintain internal stability is determined by the ability of individual organisms to adjust their physiology or behavior to change. The success with which an organism copes with environmental changes is determined by its ability to produce reproducing offspring. The size and success of a population depends upon the collective ability of organisms to reproduce and maintain their numbers in a particular environment. Those organisms that adjust best contribute most to future generations because they have the greatest number of progeny in the population (Smith, 1980; Billings, 1978; Woodwell, 1970; Odum, 1971).

The capacity of organisms to withstand injury from weather extremes, pesticides, acidic deposition or polluted air follows the principle of limiting factors (Billings, 1978; Odum, 1971; Moran et al., 1980; Smith, 1980). According to this principle, for each physical factor in the environment there exists for each organism a minimum and a maximum limit beyond which no members of a particular species can survive. Either too much or too little of a factor such as heat, light, water, or minerals (even though they are necessary for life) can jeopardize the survival of an individual and, in extreme cases, a species (Billings, 1978; Smith, 1980; Boughey, 1971; Odum, 1971). The range of tolerance (see Figure 7-2) of an organism may be broad for one factor and narrow for another. The tolerance limit for each species is determined by its genetic makeup and varies from species to species for the same reason. The range of tolerance also varies depending on the age, stage of growth, or growth form of an organism. Limiting factors are, therefore, those which, when scarce or overabundant, limit the growth, reproduction, and/or distribution of an organism (Billings, 1978; Smith, 1980; Boughey, 1971; Odum, 1971; Moran et al., 1980). The increasing acidity of water in lakes and streams is such a factor.

Organisms can exist only within their range of tolerance. Some populations of organisms, annual plants, insects, and mice, for example, respond rapidly to environmental change. They increase in numbers under favorable conditions and decline rapidly when conditions are unfavorable. Populations of other organisms, such as trees and wolves, fluctuate less in response to favorable or unfavorable conditions by showing little variation in the rates of reproduction and death. Adaptation is the ability of an organism to conform to its environment. Ecosystem stability ultimately is based on the adaptability of the organisms that compose it. Stability may be associated with the ability of a system to return to an equilibrium state after a temporary disturbance (Holling, 1973; May, 1973). The less it

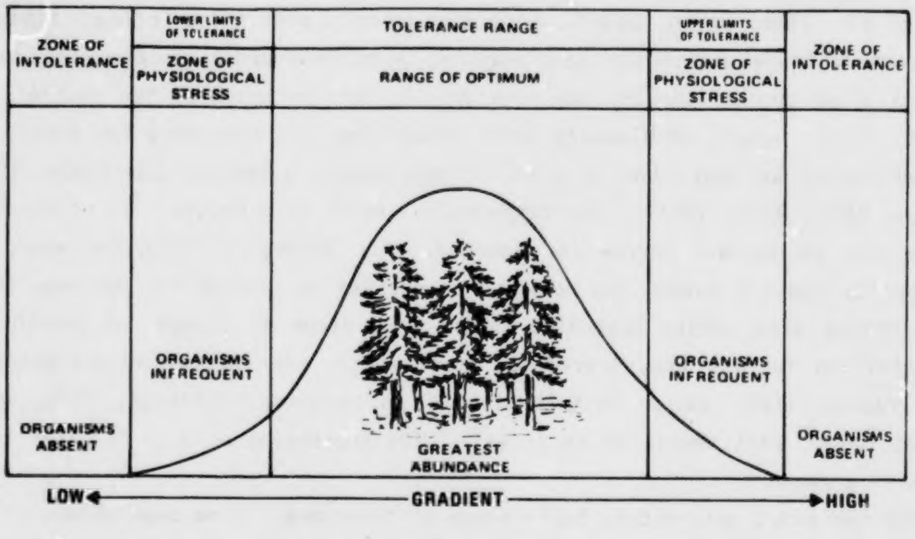

ZONE OF INTOLERANCE
LOWER LIMITS OF TOLERANCE
ZONE OF PHYSIOLOGICAL STRESS
TOLERANCE RANGE
RANGE OF OPTIMUM
UPPER LIMITS OF TOLERANCE
ZONE OF PHYSIOLOGICAL STRESS
ZONE OF INTOLERANCE
ORGANISMS ABSENT
ORGANISMS INFREQUENT
GREATEST ABUNDANCE
ORGANISMS INFREQUENT
ORGANISMS ABSENT
LOW
GRADIENT
HIGH

Figure 7-2. Law of tolerance.

Source: Adapted from Smith (1980).

varies from and the faster it returns to its original state, the more stable the system (Smith, 1980). Stability also involves persistence, the ability of the populations of an ecosystem to persist through time. Persistence involves resilience, the ability of an ecosystem to absorb changes. Although individual populations within a system may fluctuate greatly in response to environmental changes, the system may be highly resilient (Holling, 1973; Smith, 1980). Contrasted with resilience is resistance, the ability of a system, because of its structure, to resist changes from disturbances. Typically, the most resistant ecosystems have large living components, trees for example, and store nutrients and energy in the standing biomass. Resistant systems such as forests, once highly disturbed, are very slow in returning to their original state (Smith, 1980).

Aquatic ecosystems that lack components in which energy and nutrients may be stored for long periods of time usually are not very resistant to environmental changes (Smith, 1980). For example, an influx of pollutants, such as effluents from sewage disrupts the system because more nutrients enter the system than it can handle. However, since the nutrients are not retained or recycled within the system it returns to its original state in a relatively short time after the perturbation is removed.

No barriers exist between the various environmental factors, or between an organism or biotic community and its environment. Because an ecosystem is a complex of interacting components, if one factor is changed, almost all will change eventually. "The ecosystem reacts as a whole. It is practically impossible to wall off a single factor or organism in nature and control it at will without affecting the rest of the ecosystem. Any change no matter how small is reflected in some way throughout the ecosystem: no 'walls' have yet been discovered that prevent these interactions from taking place" (Billings, 1978).

Continued or severe perturbation of an ecosystem can overcome its resistance or prevent its recovery, with the result that the original ecosystem will be replaced by a new system. In the Adirondack Mountains of New York State, eastern Canada, and parts of Scandinavia, the original aquatic ecosystems have been and are continuing to be replaced by ecosystems different from the original due to acidification of the aquatic habitat. Forest ecosystems appear to be more resistant thus far, because changes due to stress from acidifying substances have not been detected.

7.2 CAUSES OF ACIDIC PRECIPITATION

7.2.1 Emissions of Sulfur and Nitrogen Oxides

The generally held hypothesis is that increased emissions of sulfur and nitrogen compounds are largely responsible for the acidity of precipitation (Smith, 1872; Bolin et al., 1972; Likens, 1976). The emissions of the sulfur and nitrogen compounds involved in the acidification are attributed chiefly to the combustion of fossil fuels. Emissions from natural sources can also be involved; however, in highly industrialized areas emissions from manmade sources usually exceed those from natural sources (see Chapter 4). (See Chapter 5 for environmental concentrations of sulfur compounds.)

After 1900 there was a nearly exponential increase in the consumption of gas and oil in the United States (see Figure 7-3). Although the total consumption of coal has not increased greatly since about 1925, the consumption of oil and gas has continued to rise precipitously, thus overshadowing coal as the dominant fuel source during the past 50 years (Hubbert, 1976). Within this overall increase in fossil-fuel use, there have been shifts in the pattern of consumption. Whereas formerly a considerable proportion of coal was used for transportation and heating, these functions have since been taken over by oil and gas. Coal is now predominantly devoted to electric power generation (Figure 7-4). In fact, electric power generation is the primary factor accounting for an absolute increase in coal consumption over the past two decades. (The decline in the use of coal in the 1930s was due to the general economic depression, and the decline in the 1950s was due to the availability of relatively inexpensive oil and gas.) Approximately 550 MM (million metric) tons (National Research Council, 1978b) were used per year during 1918-1928 compared to 672 MM tons/year during 1979 (Hamilton, 1980). There was, however, a seasonal shift in the pattern of coal consumption. Summer coal consumption has increased since 1960 because of increased usage of electricity in air conditioning, while winter consumption has decreased due to the use of alternative fuels.

These changes in the pattern of fuel use have been accompanied by changes in the pattern of pollutant emissions. Figure 7-5A and 7-5B illustrate the rise since 1940 in emissions of sulfur and nitrogen oxides, the primary gaseous pollutants resulting from the combustion of fossil fuels (See also Chapter 4). Although there has been a net increase in both categories, the more consistent rise has been in emissions of nitrogen oxides. Almost all (93 percent) emissions of sulfur oxides in the United States arise from stationary point sources, principally industrial and power plant stacks. Nitrogen oxide pollutants, on the other hand, originate about 60 percent from transportation (mobile) sources and 30 percent from stationary sources, which include not only industrial and power plants, but residential and institutional heating equipment as well (U.S. Environmental Protection Agency, 1980). (see Chapter 5 of Air Quality Criteria for Oxides of Nitrogen for a more detailed discussion.)

The geographic distributions of sources of the presumed gaseous precursors of acidic precipitation are depicted in Figures 7-6 and 7-7. Clearly, the main sources of sulfur oxides in the United States are in the eastern half of the country, particularly the northeastern quadrant. Major nitrogen oxide sources also show a tendency to be concentrated somewhat in the Northeast. Chapter 4 should be consulted for a more detailed account of the sources and emissions of sulfur oxides.

7.2.2 Transport of Nitrogen and Sulfur Oxides

Among the factors influencing the formation as well as the location where acidic deposition occurs is the long-range transport of nitrogen and sulfur oxides. Neither the gases nor their transformation products always remain near the sources from which they have been emitted.

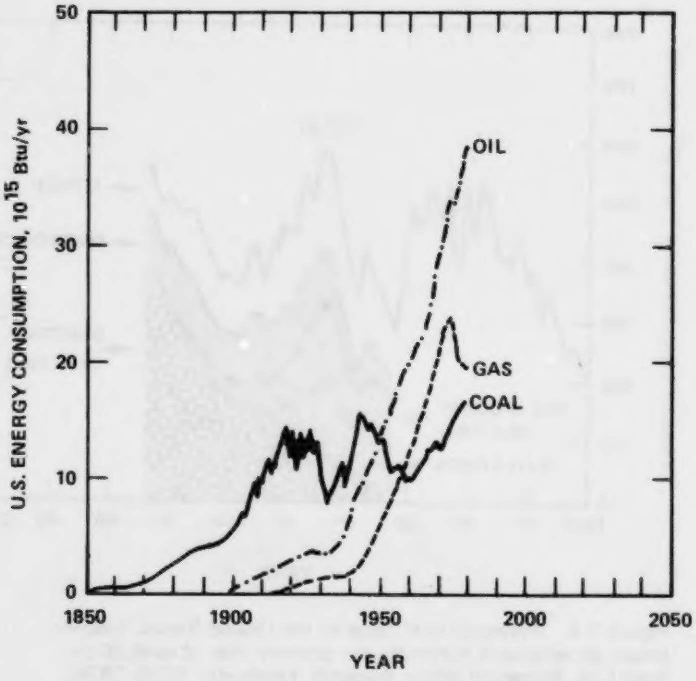


Figure 7-3. Historical patterns of fossil fuel consumption in the United States

Source: Adapted from Hubbert (1976).

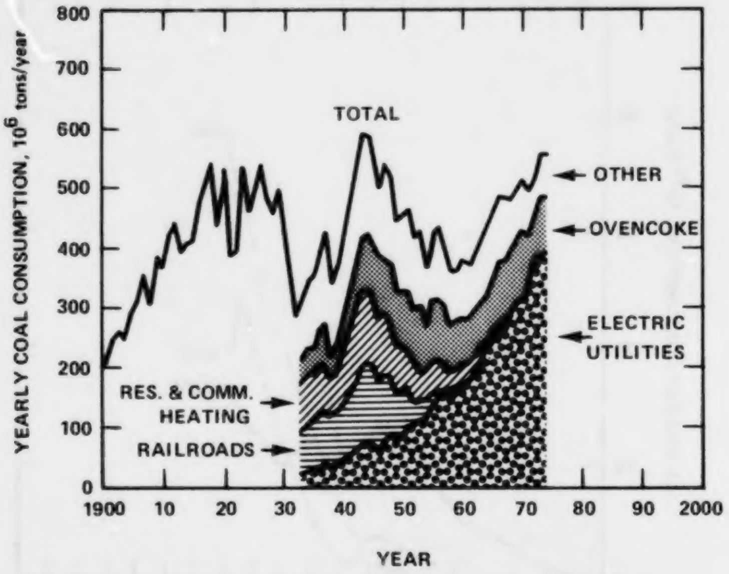
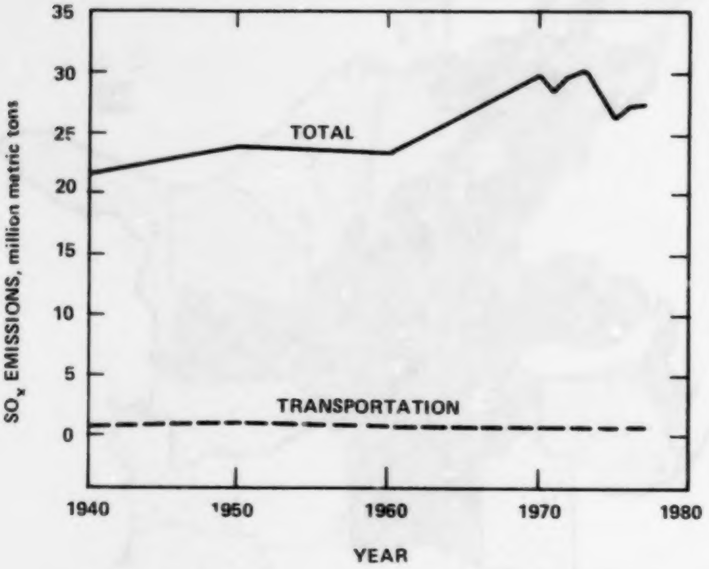


Figure 7-4. Forms of coal usage in the United States. Electric power generation is currently the primary user of coal. (Data from U.S. Bureau of Mines, Minerals Yearbooks 1933--1974).

Source: U.S. Bureau of Mines (1954, 1976).



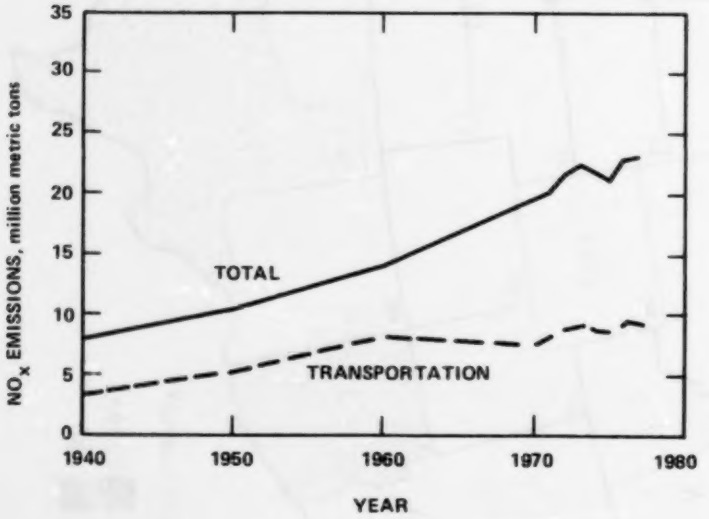


Figure 7-5a. Trends in emissions of sulfur dioxides.

Figure 7-5b. Trends in emissions of nitrogen oxides.

Source: Office of Air Quality Planning and Standards (1978).

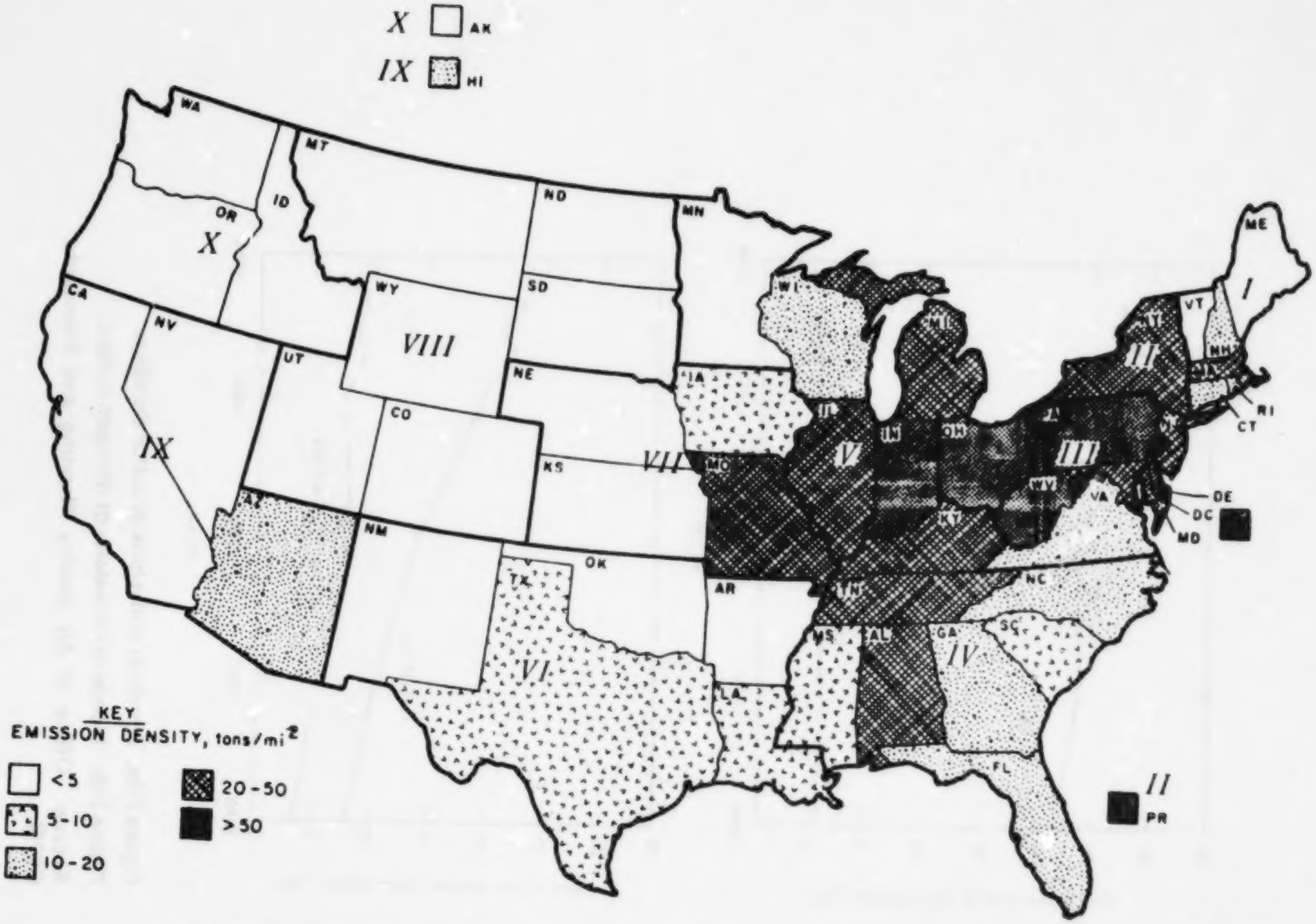

X AK
IX HI
WA
OR
CA
ID
NV
MT
WY
UT
AZ
CO
NM
ND
SD
NE
KS
OK
TX
MN
IA
MO
AR
LA
WI
IL
MI
IN
OH
KY
TN
MS
AL
GA
FL
SC
NC
VA
WV
PA
NY
VT
NH
ME
NJ
RI
CT
DE
DC
MD
PR
I
II
III
IV
V
VI
VII
VIII
IX
X
KEY
EMISSION DENSITY, tons/mi^2
<5
5-10
10-20
20-50
>50

Figure 7-6. Characterization of U.S. SO_x emissions density by state. (Roman numerals indicate EPA Regions.)

Source: U.S. Dept. of Energy (1981).

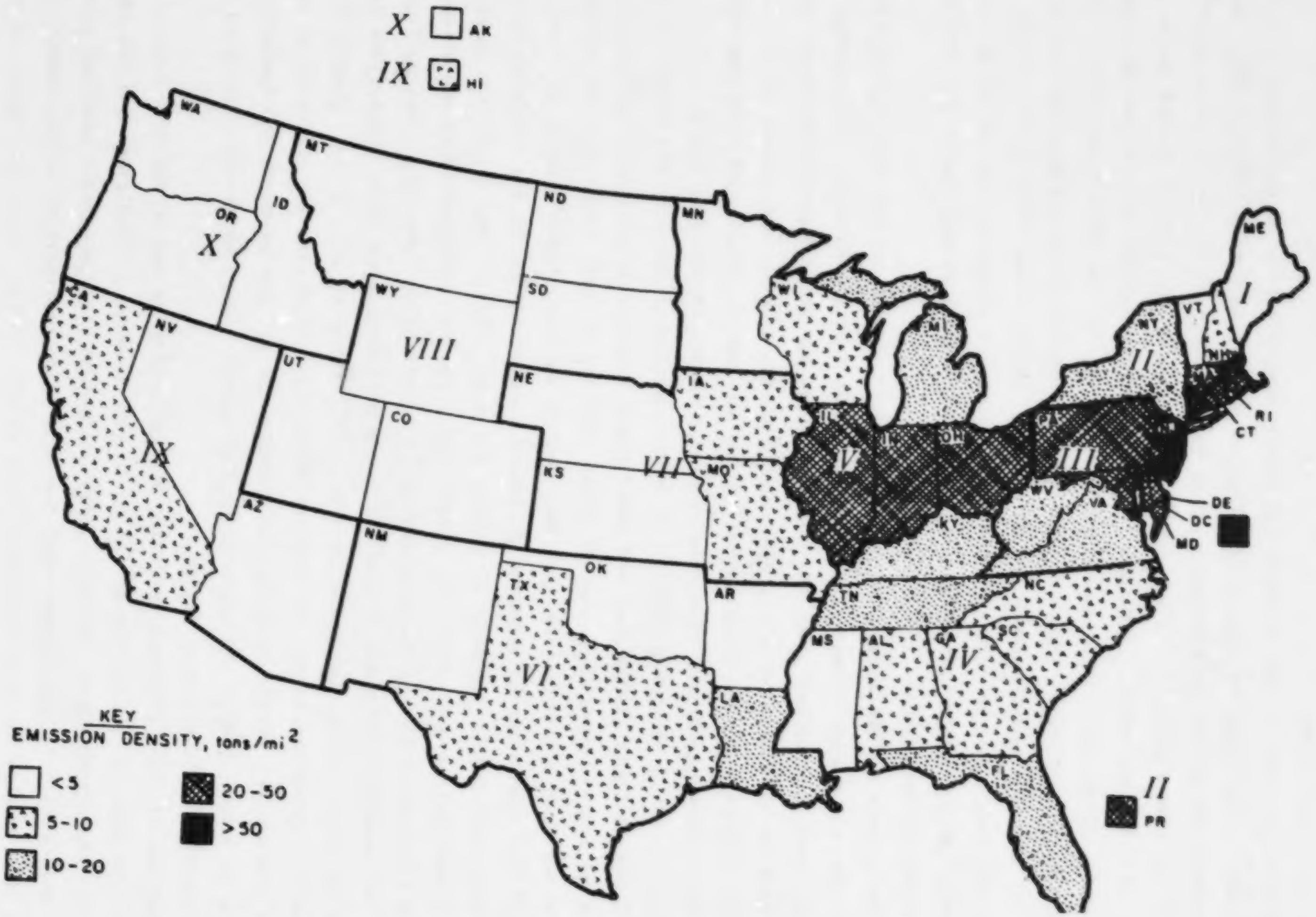

X AK
IX HI
WA
OR
X
ID
MT
ND
MN
CA
NV
WY
VIII
SD
WI
MI
NY
VT
NH
ME
I
II
UT
NE
IA
IL
IN
OH
PA
III
RI
CT
CO
KS
VII
MO
IX
V
WV
VA
DE
DC
MD
KY
AZ
NM
OK
TX
AR
TN
NC
MS
AL
GA
SC
IV
VI
LA
FL
II
PR
KEY
EMISSION DENSITY, tons/mi²
<5
5-10
10-20
20-50
>50

Figure 7-7. Characterization of U.S. NO_x emissions density by state. (Roman numerals indicate EPA Regions.)

Source: U.S. Dept. of Energy (1981).

They may be transported for long distances downwind (Altshuller and McBean, 1979; Pack et al., 1978; Cogbill and Likens, 1974). (See Chapter 6 for a detailed discussion of transport and transformation of sulfur oxides.)

The geographic picture of the problem of acidic precipitation in North America can be better understood in the light of some information on prevailing wind patterns. Winds transport the precursors of acidic precipitation from their points of origin to areas where the acidified rain and snow eventually fall. Prevailing winds in the Eastern United States tend to be from the west and southwest. Atmospheric pollutants, therefore, are carried in a generally northeasterly direction. Thus, pollution originating in the Ohio River Valley can be carried toward the New England States. Seasonal meteorological patterns, however, can modify the direction of windflow, particularly in the summer. The Maritime Tropical air masses from the Gulf of Mexico that occur in late summer have the greatest potential for the formation and transport of high concentrations of sulfate into the Northeastern United States and into eastern Canada (Altshuller and McBean, 1979).

Cogbill and Likens (1974) associated acidic rainfall in central New York during 1972-73 with high altitude air masses transported into the region from the Midwest. They stated that the NO_x and SO_2 that is involved in acidic rain formation may be transported distances of 300 to 1500 km. Reports by Miller et al. (1978), Wolff et al. (1979), and Galvin et al. (1978) all support the concept that the trajectories of the air masses which come from the Midwest carry sulfur and nitrogen compounds that acidify precipitation in New York State.

A significant, though disputed factor, in this transport picture is the height at which the pollutants are emitted. Industrial and power plant smokestacks emit their effluents into the atmosphere at higher elevations than do motor vehicles or most space heating equipment. In fact, there has been a trend since the 1960s toward building higher stacks as a means of dispersing pollutants and thereby reducing pollutant concentrations in the vicinity of power plants, smelters, and similar sources (Grennard and Ross, 1974). The result has been that sulfur and nitrogen oxides are carried by prevailing winds for long distances and allowed to diffuse over greater areas through the atmosphere. Concomitantly, long-range transport allows greater time for chemical reactions to convert these pollutant gases into particulate forms. (Eliassen and Saltbones, 1975; Smith and Jeffrey, 1975; Prahm et al., 1976). Chapter 6 discusses the chemical transformations, wet and dry deposition, transport and diffusion of sulfur oxides in the atmosphere. Sulfur dioxide and nitrogen oxides are oxidized and hydrolyzed in the atmosphere to nitric (HNO_3) and sulfuric (H_2SO_4) acids. These acids are considered to be the main components of acidic precipitation.

The mechanisms of these chemical reactions are quite complex and depend on a host of variables ranging from physical properties of the pollutants to weather conditions and the presence of catalytic or interacting agents (Fisher, 1978). Although the atmospheric chemical processes are not well understood, it does appear that the long-range transport of sulfur compounds can cover 1000 to 2000 km over three to five days (Pack et al., 1978). Thus, the impact of sulfur pollutants in the form of acidic precipitation may be far removed from their points of origin. It is not yet clear whether nitrogen oxide pollutants may be transported distances comparable to that of sulfur compounds or are local in origin (Pack, 1978); in the Northeast, however, nitrates are currently thought to contribute 15 to 30 percent of the acidity of polluted precipitation. This estimate has increased over the past few years and is expected to increase still further in the future (Robinson et al., 1978).

Evidence from northern Europe (Odén, 1968) also supports the idea that acidic rainfall is a large-scale regional problem involving long distances between emission sources and deposition of acidic precipitation. The acid rains that have received intensive study in southern Scandinavia have been shown to result primarily from emissions of nitrogen and sulfur oxides in Great Britain and the industrial regions of continental Western Europe, e.g., Holland, Belgium, and West Germany (Brosset, 1973).

7.2.3 Formation

Precipitation is that portion of the global water cycle by which water vapor from the atmosphere is converted to rain or snow and then deposited on the earth surfaces (Smith, 1980). Water moves into the atmosphere by evaporation and transpiration (water vapor lost by vegetation). Once it reaches the atmosphere, the water vapor is cooled, then condenses on solid particles and soon reaches equilibrium with atmospheric gases. One of the gases is carbon dioxide. As carbon dioxode dissolves in water, carbonic acid (H_2CO_3) is formed. Carbonic acid is a weak acid and in distilled water only dissociates slightly, yielding hydrogen ions and bicarbonate ions (HCO_3^-). When relatively pure water is in equilibrium with normal atmospheric concentrations and pressures of carbon dioxide, the pH of rain and snow is approximately 5.6 (Likens et al., 1979).

The pH of precipitation may vary and become more basic or more acidic depending on substances in the atmosphere. Dust and debris may be swept from the ground and into the atmosphere in small amounts where it can become a component of rain. The amounts of the various substances in the atmosphere originating from seawater, desert sands, volcanic islands, or vegetated land influence the chemistry of natural precipitation. In regions with calcareous soils, calcium and carbonate may enter precipitation as dust, subsequently increasing the pH of rain or snow to 6.0 or above (Likens et al., 1979). Soil particles are usually slightly basic in distilled water and release positive ions, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), and sodium (Na^+) into solution. Bicarbonate usually is the corresponding negative ion. Decaying organic matter adds gaseous ammonia to the atmosphere. Ammonia gas in rain or snow forms ammonium ions (NH_4^+) and tends to increase the pH. In coastal areas, sea spray plays a strong role in the chemistry of precipitation. The important ions entering into precipitation--sodium, magnesium, calcium, potassium, and the anions chloride (Cl^-) and sulfate (SO_4^{2-})--are also those most abundant in ocean water (Likens, 1976; Likens et al., 1979).

Gases, in addition to CO_2, which enter precipitation are ammonia, sulfur dioxide (SO_2) and the nitrogen oxides (NO_x). Sulfur gases originating from natural sources (e.g., volcanoes and swamps) may also enter precipitation. In the wet atmosphere, SO_2 can be oxidized to sulfuric acid (Likens, 1976; Likens et al., 1979). Strong acids dissociate completely in dilute aqueous solutions and may lower the pH of precipitation to less than 5.6. Rain or snow with a pH below 5.6 has been arbitrarily considered acidic precipitation by many scientists (Galloway and Cowling, 1978; Wood, 1975; Likens et al., 1979).

The most important natural sources of atmospheric sulfur are biologically reduced compounds coming from lake and sea bottoms, marshes, swamps, polluted estuaries, streams, tidal basins, and decaying vegetation. Such reduction occurs most readily under oxygen deficient conditions when organic matter is present (Cullis and Hirschler, 1980). It is virtually impossible to measure or calculate the quantities of volatile sulfur compounds emitted from biogenic sources, mainly due to lack of quantitative information concerning their reactions in the atmosphere (Cullis and Hirschler, 1980). Hydrogen sulfide, assumed initially to be the predominant reduced sulfur compound, reacts very slowly with oxygen in the absence of catalysts, but is oxidized photochemically (Eggleton and Cox, 1978). Estimates for the life time of H_2S near the Earth's surface range from 2 hours (Cadle and Ledford, 1966) to nearly 4 days (Friend, 1973). Dimethyl sulfide has been shown to be present in considerably higher concentrations above a pond (Rasmussen, 1974); however, it is much less readily oxidized than H_2S (Cadle, 1976). Biogenic sulfur emissions are much higher over the oceans than land (Cullis and Hirschler, 1980). (See also Chapter 4.)

7.2.3.1 Composition and pH of Precipitation--Sulfur and nitrogen compounds are chiefly responsible for the excess acidity of precipitation. Continuous measurement of pH in rain by Likens et al. (1972) for the Hubbard Brook Experimental Forest in New Hampshire from 1964 to 1971 indicated the precipitation was acid with an annual weighted average pH range of 4.03 to 4.19. (A weighted average takes into account the amount of rain as well as its composition.) Cogbill and Likens (1974), analyzing precipitation from the Ithaca area and Hubbard Brook, which consistently had a pH of less than 4.4, reported that their analysis of precipitation showed that 65 percent of the acidity was due to H_2SO_4, 30 percent to HNO_3, and less than 5 percent was due to HCl.

In 1976, Likens (1976) reported that the continued monitoring of precipitation at the Hubbard Brook Forest through 1974 indicated the average annual weighted pH for the years 1964-1974 ranged from 4 03 to 4.21. There was a downward trend in annual pH values between 1964-65 and 1970-71 followed by an upward trend until 1973-74, but no statistically significant trend was noted for the 1964-74 period; however, pH values of 2.1 and 3.0 were observed for individual storms at various locations. There was an increase in nitric acid in the precipitation (rain and snow) falling there. This change in the composition of acidic precipitation suggests that the sources of nitrogen oxide emissions increased while those for sulfur oxides remained constant.

The acidity of precipitation is a reflection of the hydrogen ions in precipitation. The contribution of sulfate and nitrate anions has changed with time, and analysis indicates that the nitrate anion makes up an ever-increasing fraction of the total negative ion equivalents. Following the reasoning of Granat (1972), Likens et al. (1976) found [assuming $2H^+$ per SO_4^{2-} ion as in H_2SO_4 or one H^+ ion per NO_3^- as in (HNO_3)] that the contribution of sulfate to acidity declined from 83 to 66 percent of the total acidity between 1964 to 1974 at Hubbard Brook, and the contribution of nitrate increased from 15 percent to 30 percent of the total during the same period. Furthermore, increased annual input of H^+ was closely correlated with increased input of nitrate, but there was little correlation between H^+ input and sulfate input.

Data for nitrate, ammonium, and sulfate in rain at Ithaca and Geneva, New York, constitute the longest record of precipitation chemistry in the United States (Likens, 1972). Data are available from 1915 to the present, but long gaps exist in the measurements, especially at the Geneva site. Figures 7-8 (A) to (C) show that marked changes in composition have occurred at Ithaca: a gradual decline in ammonium, an increase in nitrate beginning around 1945, and a marked decrease in sulfate starting between 1945 and 1950. Early data for Ithaca showed higher concentrations of sulfate in winter than in summer, presumably because of greater local burning of coal in winter. Data for 1971 showed the reverse trend, however, with nearly half the annual sulfate input occurring during the months of June to August. Likens (1972) concluded that, despite deficiencies in the historical data and questions concerning their reliability, the trends are real and can be explained by changes in fuel consumption patterns, i.e., natural gas began to replace coal for home heating near the time of the shifts in precipitation chemistry. On the basis of United States Geological Survey data for nine stations, Likens (1976) reported a sharp increase in nitrate concentrations in New York State during the past decade (Figure 7-8 [D]).

Data for eastern North America (the U.S. east of the Mississippi River) indicate a roughly three-fold increase in nitrate in rainfall since 1955, whereas sulfate in rain has roughly doubled in this period. According to Nisbet (1975), sulfate/nitrate ratios in rainfall averaged about 4 in the Eastern United States in 1955-1956, but the average ratio had fallen to about 3 in 1972-1973. Nisbet calculated that the fraction of H^+ deposition attributable to nitrate rose from 19 percent in 1955-1956 to 24 percent in 1972-1973, while the deposition attributable to H_2SO_4 decreased from 80 to 73 percent.

Lindberg et al. (1979) noted that SO_4^{2-} and H^+ were by far the dominant constituents of precipitation at the Walker Branch Watershed, Tennessee. Comparison with the annual average concentration of major elements in rain at the Walker Branch Watershed on an equivalent basis indicated that H^+ constitutes approximately 50 percent of the cationic strength and trace elements account for only 0.2 percent. Sulfate constituted approximately 65 percent of the anionic strength and on an equivalent basis was 3.5 times more concentrated than NO_3^-, the next

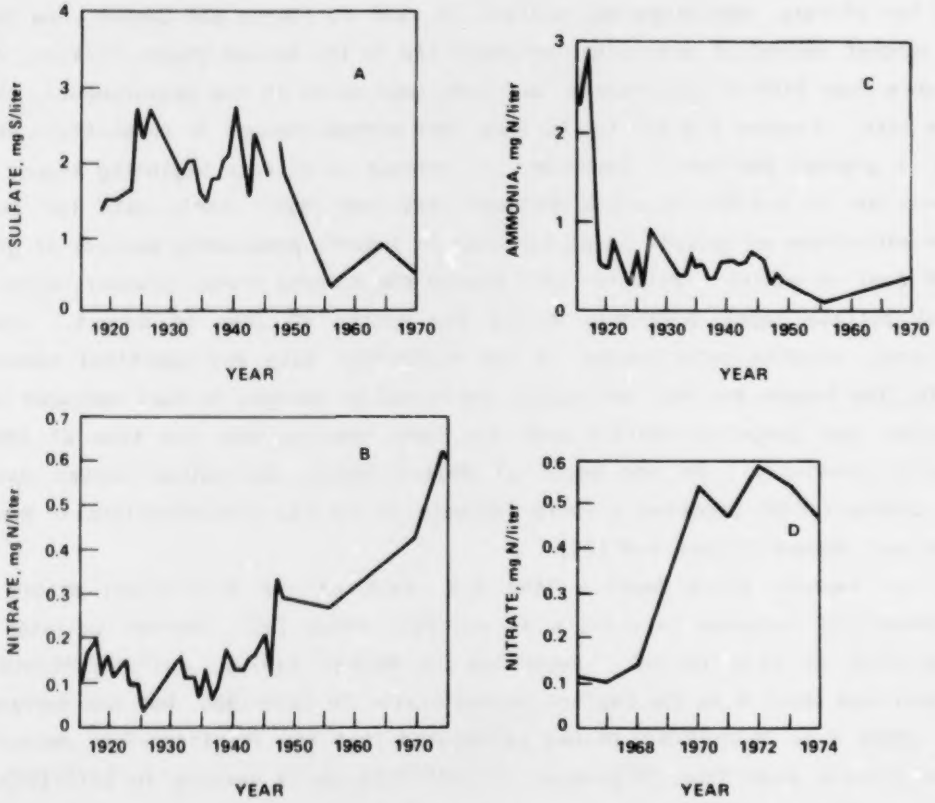


Figure 7-8. Trends in mean annual concentrations of sulfate, ammonia, and nitrate in precipitation. (A), (B), and (C) present long-term data for Ithaca, New York; (D) presents data for eight years averaged over eight sites in New York and one in Pennsylvania. One point in (A), for 1946-7, is believed to be an anomaly (see Likens, 1972, for discussion).

Source: (A), (B), and (C) modified from Likens (1972); (D) modified from Likens (1976).

most abundant anion. The incident precipitation for the 2-year (1976-1977) period was described as "a dilute mineral acid solution," primarily H_2SO_4, at a pH approximating 4.2 and containing relatively minor amounts of various trace salts (Lindberg et al., 1979). In Florida, Hendry (1977) and Hendry and Brezonik (1980) found that the relative proportions of sulfate, nitrate and chloride ions in rainfall at Gainesville, Florida, during 1976, were 69 percent, 23 percent and 8 percent, respectively.

Based on most reports, sulfate (SO_4^{2-}) appears to be the predominant anion in acidic precipitation in the Eastern United States. In California, however, nitrate (NO_3^-) seems to predominate. Liljestrand and Morgan (1978) reported that their analyses of acidic rainfall collected from February 1976 to September 1977 in the Pasadena, CA area showed that the volume-weighted mean pH was 4.0, with nitric acid being 32 percent more important as a source of acidity than sulfuric acid. The major cations present were H^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+} while the major anions were Cl^-, NO_3^- and SO_4^{2-}. McColl and Bush (1978) also noted the strong influence of nitrate on rain in the Berkeley, CA, region. However, they note that in bulk precipitation (wet plus dry fall-out) sulfate (SO_4^{2-}) constituted 50 percent of the total anions.

Nearly all of the nitrate in rainfall is formed in the atmosphere from NO_x. Little is derived from wind erosion of nitrate salts in soils. Similarly, nearly all of the sulfate in rainfall is formed in the atmosphere from SO_2 (Galloway, 1978). Thus, all atmospherically derived nitrate and sulfate can contribute to the acidification of precipitation, since H^+ is associated stoichiometrically with the formation of each. A second stoichiometric process that affects the acidity of rain is the reaction of nitric and sulfuric acids with ammonia or other alkaline substances (e.g., dust particles) in the atmosphere to form neutral nitrate and sulfate aerosols. To the extent that such neutralization occurs, the acidity of precipitation will be reduced (National Research Council, 1978). However, since much of the ammonium ion reaching soil is converted to nitrate, these neutral salts can still have an acidifying effect on the soil. (See Section 7.3.2.1)

Seasonal fluctuations in composition as well as pH of rainfall have been reported by many workers. In addition, the pH and composition of rainfall fluctuate from event to event, within an event, from locality to locality, and from storm to storm.

In general SO_4^{2-} and H^+ concentrations in precipitation in the eastern United States are higher in the summer than in the winter. Wolff et al. (1979) found this to be true for the New York metropolitan area. Hornbeck et al. (1976) and Miller et al. (1978) both stated that a summer maximum for sulfate was associated with an increase in hydrogen ion concentration in upstate New York, the Hubbard Brook Experimental Forest in New Hampshire, and in portions of Pennsylvania. Pack (1978), using data (1977) from the four original MAP3S (Multistate Atmospheric Power Production Pollution Study) precipitation chemistry stations, plotted the weighted monthly sulfate ion concentrations shown in the figure by Lindberg, (Figure 7-9). Maximum sulfate concentrations occurred from June through August. Lindberg et al. (1979), studying wetfall deposition of sulfate in the Walker Branch Watershed, also noted summer maximum for SO_4^{2-} and H^+. Using the same MAP3S data as did Pack, they plotted weighted mean concentrations of sulfate in rain collected from November 1976 through November 1977. The peak summer concentrations at Walker Branch Watershed, Tennessee, are lower than all of the stations except remote Whiteface Mountain, New York. The regional nature of the wet deposition of sulfate is apparent. Reasons for the existence of the high summer maxima of sulfate for the Eastern United States are discussed in some detail in Chapter 5, Section 5.5.1.

Seasonal variations of nitrogen compounds and of pH in precipitation have been reported by several workers, but no simple trends are apparent (see U.S. Environmental Protection Agency Air Quality Criteria for Oxides of Nitrogen, 1982). Hoeft et al. (1972) found relatively constant levels of nitrate in rain and snow collected in Wisconsin throughout the year, but deposition of ammonia and organic nitrogen was lowest in winter and highest in spring, perhaps because of the thawing of frozen animal wastes. Haines (1976) reported large random variations, but relatively small seasonal variations, for the various forms of nitrogen in wet-only precipitation at Sapelo Island, Georgia; nitrogen concentrations were lowest during the rainy months of July and September. The highest nitrogen loadings occurred during July and were asosciated with the lowest range in pH (4.2-4.8). Hendry (1977) and Hendry and Brezonik (1980) found relatively smooth seasonal trends in ammonia and nitrate concentrations in both wet-only and bulk collections (wet- and dryfall) at Gainesville, Florida, with lowest concentrations in winter (Figure 7-10). In addition, the pH of the bulk precipitation showed no seasonal trend. Wet-only collections, however, showed the lowest pH value (4.0) during the spring and summer. The historical record suggests there has been an increase in the concentration of inorganic nitrogen in Florida over the past 20 years.

Scavenging by rainfall produces large changes in atmospheric contaminant concentrations during a given rainfall event. The decline in constituent levels is usually rapid, at least in localized convective showers; low, steady-state concentrations are usually reached within the first half hour of a rain event due to cleansing of the atmosphere by rain (Brezonik, 1975). Major ions [chloride (Cl^-) and sulfate ($SO_4^=$)], inorganic forms of nitrogen [nitrate (NO_3^-) and ammonium (NH_4^+)], total phosphorus and pH were measured in rain collected in 5-minute segments within three individual rainstorms. Initially, rapid decreases were observed for nitrate and ammonium and total phosphorus. There was also a decrease in pH from 4.65 to 4.4. Steady state concentrations were reached in 10 minutes. Two other storms sampled in the same manner showed similar but less defined patterns (Hendry & Brezonik, 1980).

Wolff et al. (1979) examined spatial, meteorological and seasonal factors associated with the pH of precipitation in the New York metropolitan area. Seventy-two events were studied

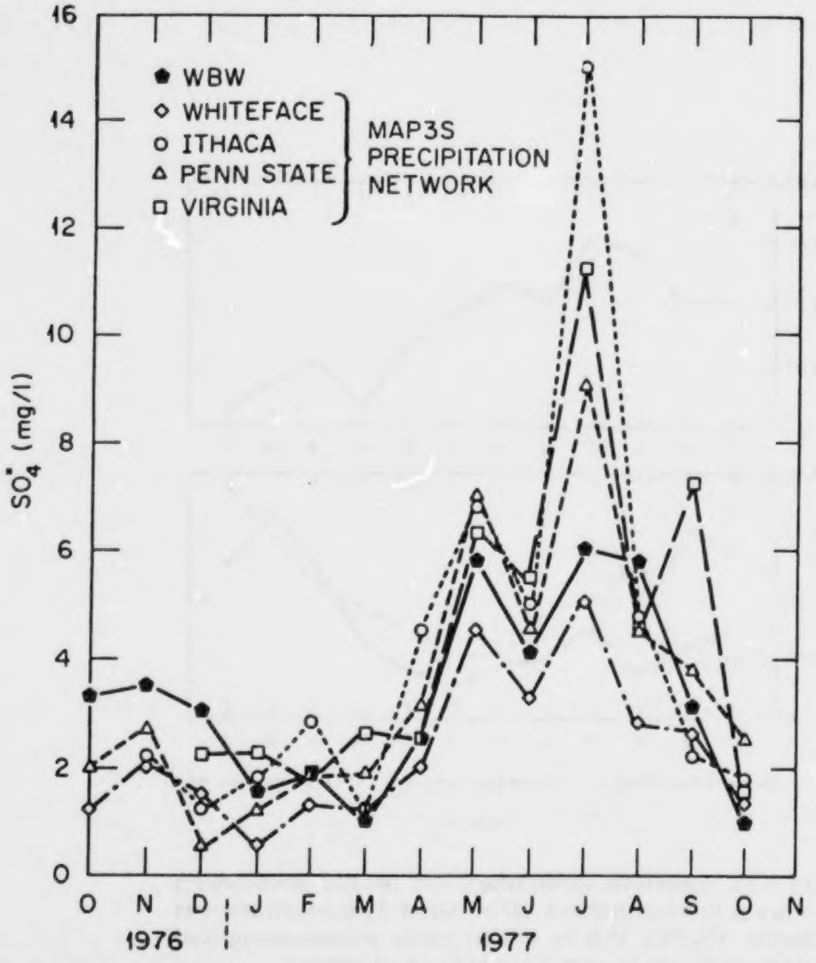


Figure 7-9. Comparison of weighted mean monthly concentrations of sulfate in incident precipitation collected in Walker Branch Watershed, Tenn. (WBW) and four MAP3S precipitation chemistry monitoring stations in New York, Pennsylvania, and Virginia.

Source: Lindberg et al. (1979).

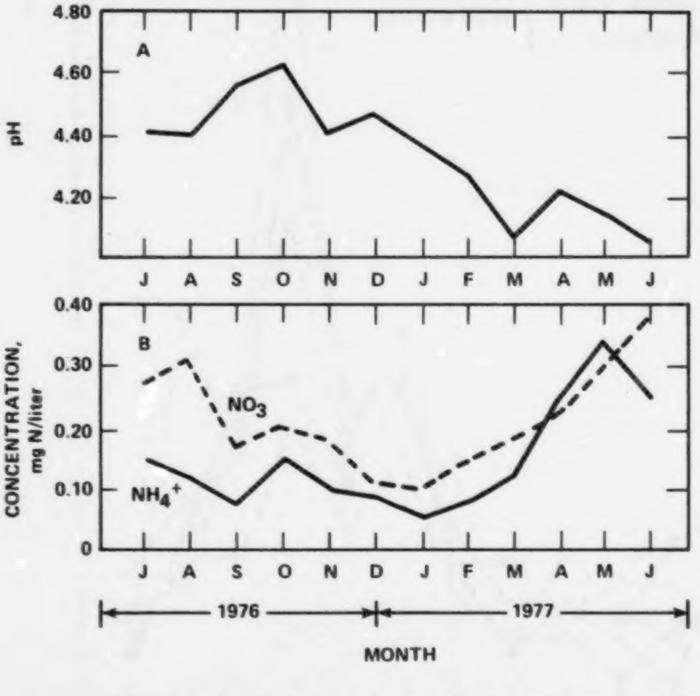


Figure 7-10. Seasonal variations in pH (A) and ammonium and nitrate concentrations (B) in wet-only precipitation at Gainsville, Florida. Values are monthly volume-weighted averages of levels in rain from individual storms.

Source: Hendry (1977).

from 1975 through 1977. There was some site-to-site variability in the hydrogen ion concentration expressed as pH values among the eight sites they studied in the Manhattan area (Table 7-2). The standard deviation for individual sites ranged between 0.20 and 0.37. They also noted that the pH varied according to storm type (Table 7-3). Storms with a continental origin have a slightly lower pH than storms originating over the ocean. The storms with trajectories from the south and southwest had the lowest pH's, while those from the north and east had the highest pH's (Wolff et al., 1979).

The mean pH of precipitation falling on the New York metropolitan area during a 2-year (1975 to 1977) study was 4.28; however, a pronounced seasonal variation was observed (Figure 7-11). The minimum pH at all sites except Manhattan was recorded during July to September, while the maximum occurred during October to December. The minimum pH in Manhattan, however, was measured between January and March and then gradually increased through the year. The lowest mean pH of 4.12 for the New York Metropolitan area occurred during the summer months (Wolff et al., 1979). In general, the pH of rain is usually lower in the summer than in the winter and is associated with the high summertime sulfate concentrations. In addition, the lowest pH's were associated with cold fronts and air mass type precipitation events. These events occur more frequently during the summer months. The lower pH's also occurred on westerly or southwesterly winds (Wolff et al., 1979).

Seasonal variations in pH measured at several sites in New York State 70 km (45 mi.) apart demonstrated a significant difference between seasons (winter had an average pH of 4.2; summer, 3.9.) but no significant difference between sites. In New Hampshire, however, six summer storms sampled at 4 sites less than 3 km (2 mi.) apart showed a significant difference (3.8 to 4.2) indicating considerable variation in pH may occur in the same storm (Cogbill 1976).

Stensland (1978, 1980) compared the precipitation chemistry for 1954 and 1977 at a site in central Illinois. The pH for the 1954 samples had not been measured, but were calculated from the data of Larson and Hettick (1956) and compared with those measured in 1977. The calculated pH for 1954 was 6.05; the pH for 1977 was 4.1. The more basic pH in 1954, according to the author, could have resulted from low levels of acidic ions (e.g. sulfate or nitrate) or from high amounts of basic ions (e.g. calcium and magnesium). Stensland suggests that the higher pH in 1954 was due to calcium (Ca^{++}) and magnesium (Mg^{++}) ions from the soil.

7.2.3.2 Geographic Extent of Acidic Precipitation--Acidic precipitation has been a reality in New York State for an undetermined period of time. Data collected by the United States Geological Survey (Harr and Coffey, 1975) are presented in Figure 7-12. The pH of precipitation has remained nearly at the same average level during the entire ten-year period; therefore, since data for the years prior to 1965 are lacking, it is difficult to determine when the pH in precipitation first began to decrease (Harr and Coffey, 1975).

TABLE 7-2. MEAN pH VALUES IN THE NEW YORK METROPOLITAN AREA (1975-1977)

Site	Mean pH	SD	No. obsd	Range
Caldwell, N.J.	4.32	0.26	50	3.35-5.60
Piscataway, N.J.	4.25	0.36	64	3.57-5.50
Cranford, N.J.	4.34	0.34	48	3.44-5.95
Bronx, N.Y.	4.31	0.37	57	3.42-5.75
Manhattan, N.Y.	4.29	0.25	39	3.80-5.50
High Point, N.J.	4.25	0.30	25	3.74-4.90
Queens, N.Y.	4.63	0.35	20	3.98-5.28
Port Chester, N.Y.	4.60	0.19	21	4.00-5.10
All sites	4.28	0.32	72	3.50-5.16

Source: Wolff et al. (1979.)

TABLE 7-3. STORM TYPE CLASSIFICATION

Type	Description of dominant storm system	No. obsd	Mean pH
1	Closed low-pressure system which formed over continental N. Amer.	22	4.35
2	Closed low-pressure system which formed in Gulf of Mexico or over Atlantic Ocean	21	4.43
3	Closed low which passed to W or N of N.Y.C.	26	4.39
4	Closed low which passed to S or E of N.Y.C.	17	4.39
5	Cold front in absence of closed low	16	4.17
6	Air mass thunderstorm	5	3.91
7	Hurricane Belle	1	5.16
8	Unclassified	6	4.31

Source: Wolff et al. (1979).

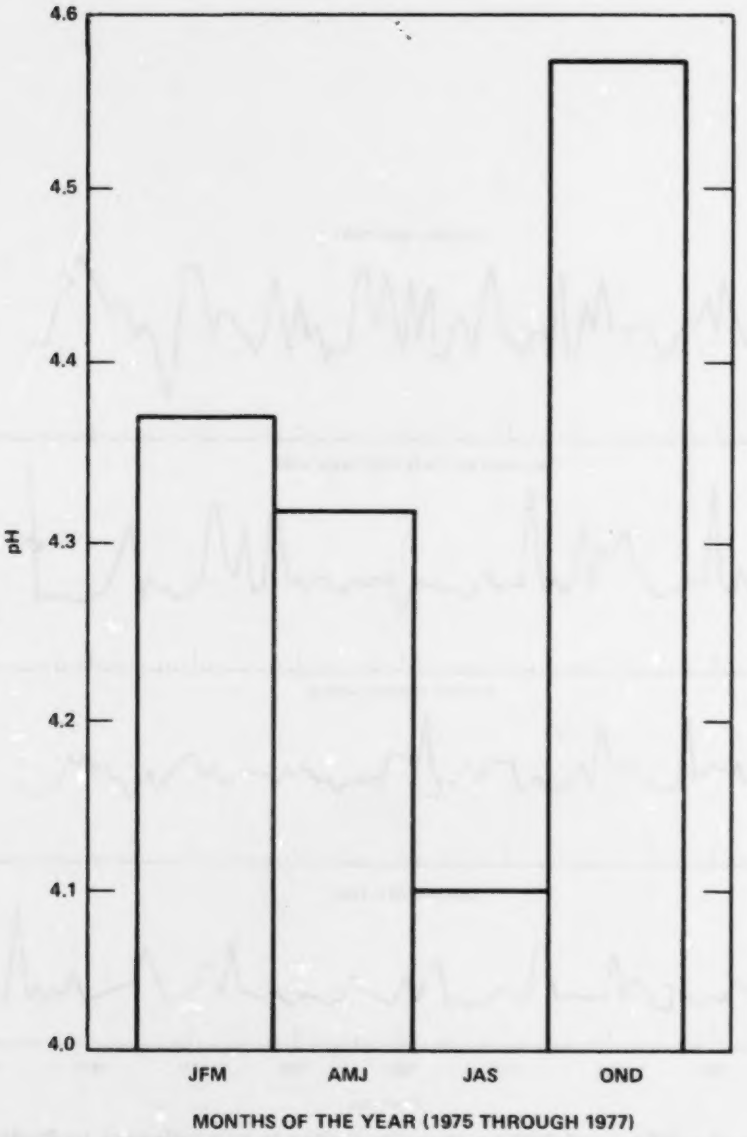


Figure 7-11. Seasonal variation of precipitation pH in the New York Metropolitan Area.
Source: Wolff et al. (1979).

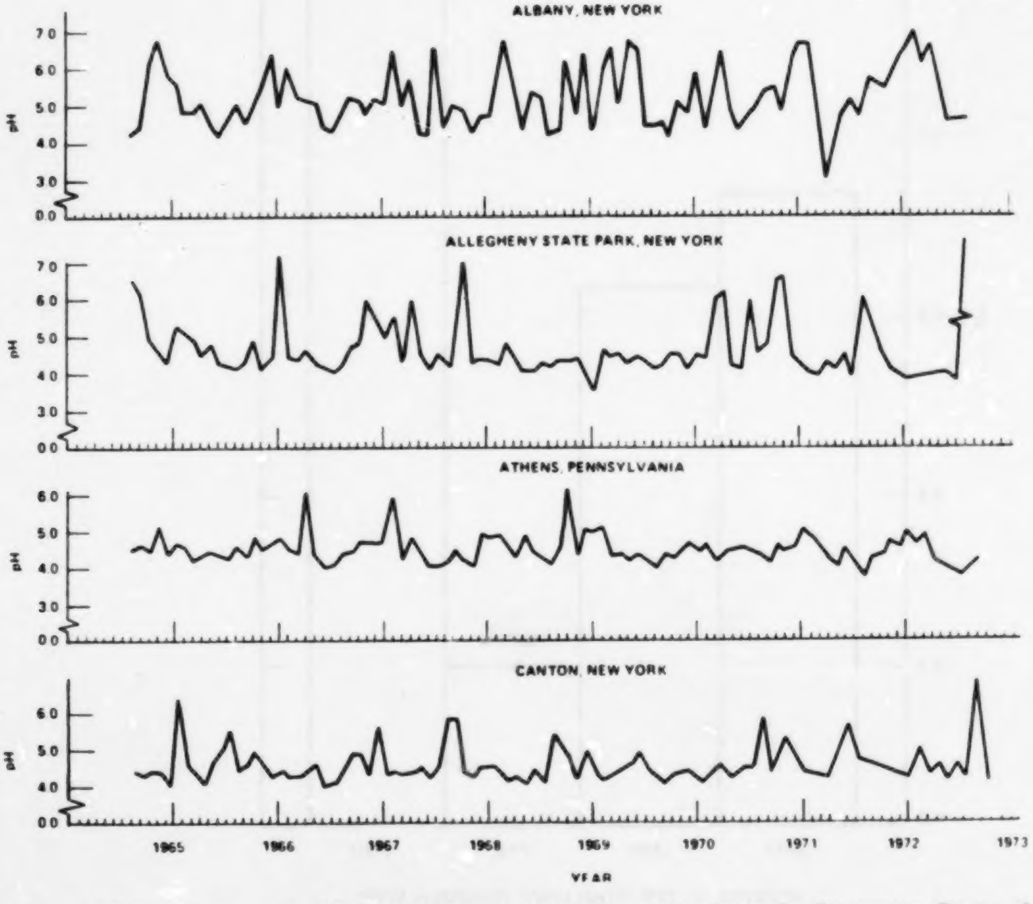


Figure 7-12. History of acidic precipitation at various sites in and adjacent to State of New York.
Source: Harr and Coffey (1975).

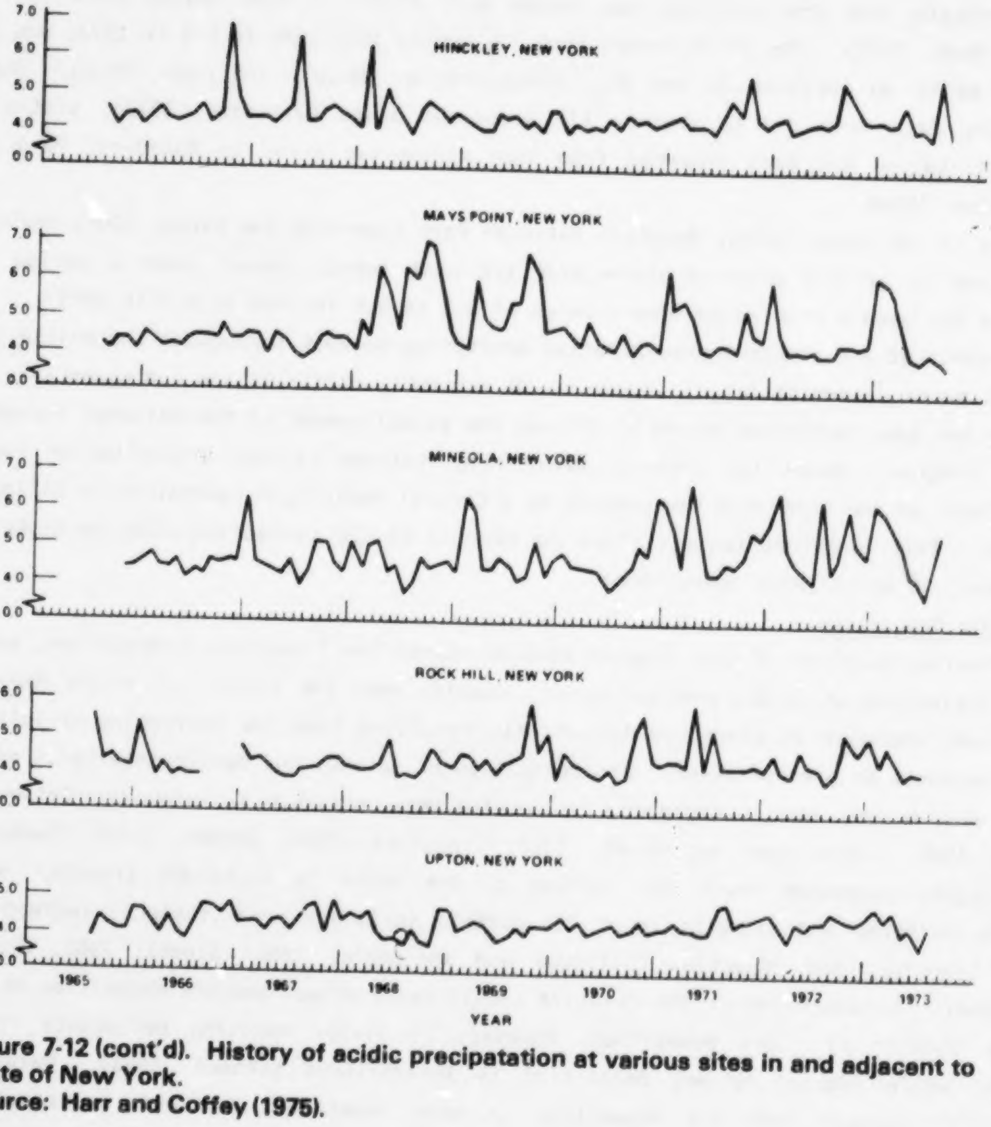


Figure 7-12 (cont'd). History of acidic precipatation at various sites in and adjacent to State of New York.
Source: Harr and Coffey (1975).

Reports indicate that precipitation is acidic in parts of the country other than the northeastern United States (See Figure 7-13.). Average pH values around 4.5 have been reported as far south as northern Florida (Likens, 1976; Hendry and Brezonik, 1980), from Illinois (Irving, 1978), the Denver area of Colorado (Lewis and Grant, 1980), the San Francisco Bay area of California (McColl and Bush, 1978; Williams, 1978), Pasadena, California (Liljestrand and Morgan, 1978), the Puget Sound area of Washington (Larson et al., 1975), and from eastern Canada (Glass et al., 1979; Dillon et al., 1978). Data from the San Francisco Bay area indicate that precipitation has become more acidic in that region since 1957-1958 (McColl and Bush, 1978). The pH decreased from 5.9 during 1957-1958 to 5.0 in 1974, and seems to be related to an increase in the NO_3^- concentration (McColl and Bush, 1978). Another report, using data from the California Air Resources Board (Williams, 1978), states that acidic precipitation has been reported from such widespread areas as Pasadena, Palo Alto, Davis, and Lake Tahoe.

Studies in the Great Smokey Mountain National Park (Herrmann and Baron, 1980) indicate a downward trend in pH has occurred there over the past twenty years. Over a period of 20 years, there has been a drop in pH from a range of 5.3 to 5.6 in 1955 to 4.3 in 1979.

The absence of a continuous precipitation monitoring network throughout the United States in the past makes determination of trends in pH extremely difficult and controversial. This shortcoming has been rectified recently through the establishment of the National Atmospheric Deposition Program. Under the program, monitoring stations collect precipitation samples, determine their pH and then send the samples to a Central Analytical Laboratory in Illinois to be analyzed. This long-term network plans to have 75 to 100 collection sites throughout the United States; 74 are already operational.

7.2.4 Acidic Deposition

The previous sections of this chapter have discussed the formation, composition, and geographic distribution of acidic precipitation. Usually when the effects of acidic deposition are discussed, emphasis is placed on the effects resulting from the scavenging of sulfur and nitrogen compounds by precipitation. Dry deposition of gaseous and particulate forms of these compounds also occurs and is beginning to receive more emphasis in research (Galloway and Whelpdale, 1980; Schlesinger and Hasey, 1980; Stensland, 1980; Sehmel, 1980; Chamberlain, 1980). Gaseous compounds reach the surface of the earth by turbulent transfer, whereas particulate sulfates and nitrates reach the earth's surface by gravitational sedimentation, turbulent transfer, and impaction (Galloway and Whelpdale, 1980; Sehmel, 1980; Hicks and Wesely, 1980). A comparison of the relative significance of wet and dry deposition is difficult (See Chapter 6). Dry deposition, however, is always removing pollutants from the atmosphere, while removal by wet deposition is intermittent (Sehmel, 1980). Marenco and Fontan (1974) suggest that dry deposition is more important than wet in removing air pollutants.

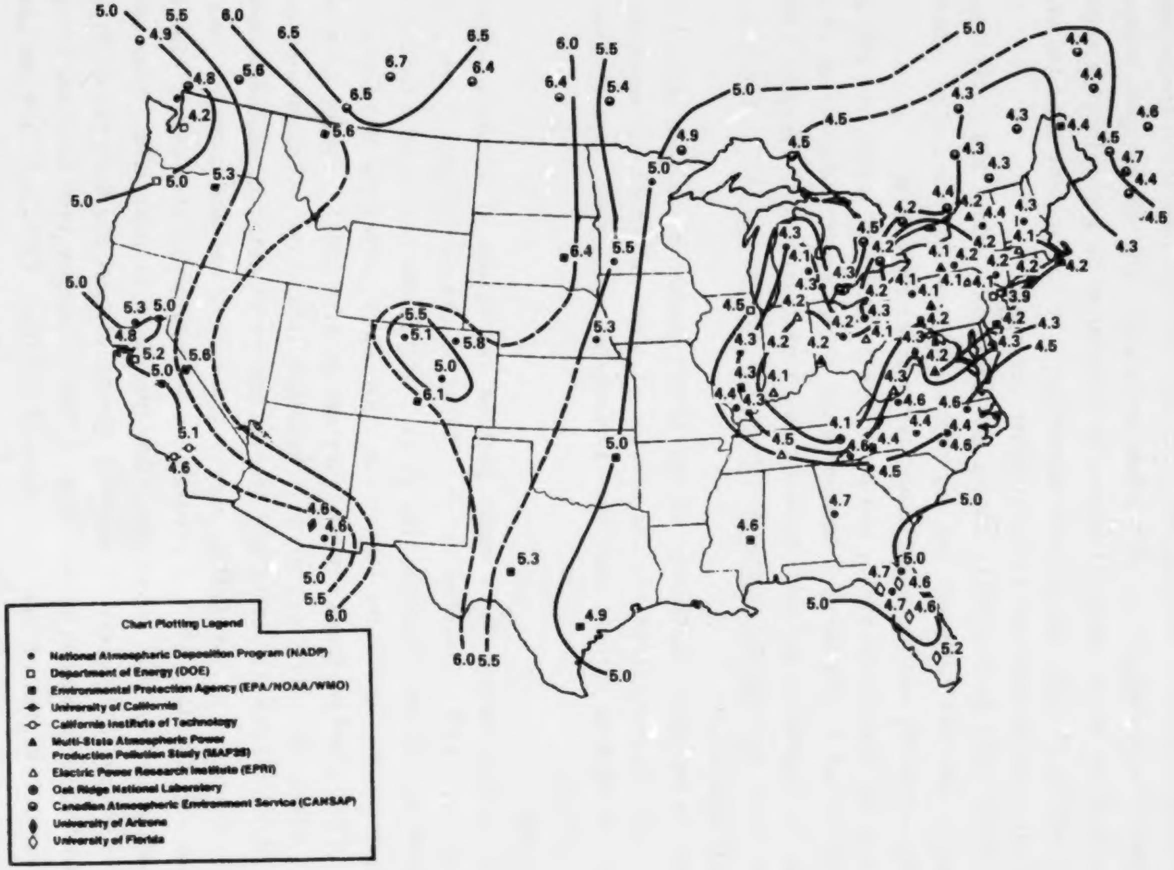


Chart Plotting Legend
● National Atmospheric Deposition Program (NADP)
□ Department of Energy (DOE)
■ Environmental Protection Agency (EPA/NOAA/WMO)
University of California
California Institute of Technology
▲ Multi-State Atmospheric Power Production Pollution Study (MAP3S)
△ Electric Power Research Institute (EPRI)
● Oak Ridge National Laboratory
Canadian Atmospheric Environment Service (CANSAP)
University of Arizona
◇ University of Florida

Figure 7-13. pH of rain samples as measured in the laboratory and used in combination with the reported amount of precipitation.

Source: Wisniewski and Keitz (1981).

Lindberg et al. (1979) have calculated the annual mass transfer rates of sulfates to the forest floor in Tennessee (Figure 7-14). Their calculations for $SO_4^{=}$ suggest wet deposition by incident precipitation to be 27 percent of the total annual flux compared with a total dry precipitation of 13 percent. The dry deposition and foliar absorption of SO_2, a very important component, is missing from this calculation. The wet and dry deposition percentages are indicative only of the relative magnitude of the two processes. The percentages, however, do point out that the effects of acidic deposition usually attributed to precipitation scavenging alone are probably a result of both wet and dry deposition. At the present time the accuracy with which dry deposition can be measured is still under question.

The studies of McColl and Bush (1978), Hendry and Brezonik (1980), and Schlesinger and Hasey (1980) also point out that both wet and dry deposition are important when considering the effects of H^+, SO_4^{2-}, and NO_3^- ions on aquatic and terrestrial receptors.

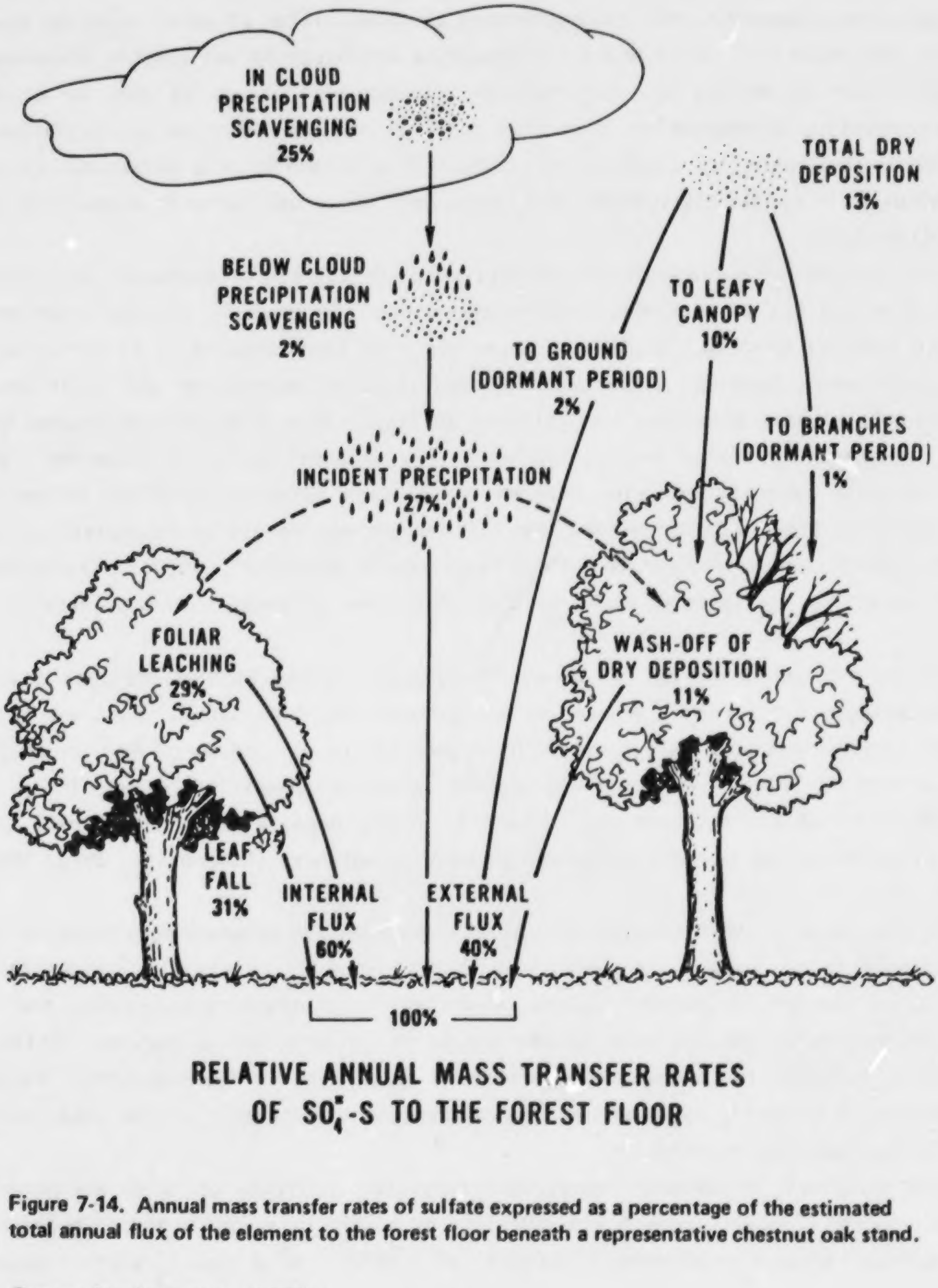
The effects of the dry deposition of SO_2 and particulate matter on vegetation and terrestrial ecosystems is discussed in Chapter 8. The processes of wet and dry deposition of sulfur oxides are discussed in Chapter 6 of this document; such processes for nitrogen oxides are discussed in Chapter 6 of Air Quality Criteria for Oxides of Nitrogen (U.S. E.P.A., 1982).

7.3 EFFECTS OF ACIDIC DEPOSITION

Acidic precipitation has been implicated in the acidification of surface waters leading to the degradation of aquatic ecosystems, in the erosion of stone buildings and monuments, and as a potential source of harm to forests and other terrestrial ecosystems. The sections that follow discuss these effects.

7.3.1 Aquatic Ecosystems

Acidification of surface waters is a major problem in regions of southern Scandinavia (Oden, 1968; Almer et al., 1974; Gjessing et al., 1976), Scotland (Wright et al., 1980a), eastern Canada (Beamish and Harvey, 1972; Dillon et al., 1978), and the Eastern United States in the Adirondack Region of New York State (Schofield, 1976 a,b,c,; Pfeiffer and Festa, 1980), Maine (Davis et al., 1978), and northern Florida (Crisman et al., 1980). Damage to fisheries is the most obvious effect of acidification on freshwater life. The disappearance of fish populations from acidified fresh water lakes and streams was first noted in southern Norway in the 1920's. In 1959, Dannevig proposed that acidic deposition was the probable cause for acidification and thus for the loss of fish populations (Leivestad et al., 1976). Subsequent studies have attempted to verify this postulate. Declines in fish populations have been related to acidification of surface waters in southern Norway (Jensen and Snekvik, 1972; Wright and Snekvik, 1978), southwestern Sweden (Almer et al., 1974), southwestern Scotland (Wright et al., 1980a), the Adirondack Region of New York State (Schofield, 1976a,b,), and the LaCloche Mountain Region in southern Ontario (Beamish and Harvey, 1972). Acidification may also have serious repercussions on other aquatic biota inhabiting these systems. Changes in the acidity and chemistry of freshwater affect the communities of organisms living there. Pertinent details of these effects are described in the following sections.


IN CLOUD PRECIPITATION SCAVENGING 25%
TOTAL DRY DEPOSITION 13%
BELOW CLOUD PRECIPITATION SCAVENGING 2%
TO LEAFY CANOPY 10%
TO GROUND (DORMANT PERIOD) 2%
TO BRANCHES (DORMANT PERIOD) 1%
INCIDENT PRECIPITATION 27%
FOLIAR LEACHING 29%
WASH-OFF OF DRY DEPOSITION 11%
LEAF FALL 31%
INTERNAL FLUX 60%
EXTERNAL FLUX 40%
100%

RELATIVE ANNUAL MASS TRANSFER RATES
OF $SO_4^=$-S TO THE FOREST FLOOR

Figure 7-14. Annual mass transfer rates of sulfate expressed as a percentage of the estimated total annual flux of the element to the forest floor beneath a representative chestnut oak stand.

Source: Lindberg et al. (1979).

7.3.1.1 Acidification of lakes and streams--Precipitation enters lakes directly as rain or snow or indirectly as runoff or seepage water from the surrounding watershed. The relative magnitude of the influents from these two sources is dependent on the surface area and volume of the lake, and the size of the watershed and its soil volume and type. In general, the watershed plays a dominant role in determining the composition of water entering the lake. As a result, the water will be strongly influenced by processes in the edaphic environment of the watershed, such as weathering, ion exchange, uptake and release of ions by plants, carbon dioxide production by vegetation, microbial respiration, and reduction and oxidation reactions of sulfur and nitrogen compounds (Seip, 1980). Precipitation as a direct source of water to the lake plays a relatively greater role when lake areas are large in comparison to the size of the watershed.

Acidification of surface waters results when the sources of hydrogen ion exceed the ability of an ecosystem to neutralize the hydrogen ion. In general, the soils and crust of the earth are composed principally of basic materials with large capacities to buffer acids. However, areas where bedrock is particularly resistant to weathering and soils are thin and poorly developed have much less neutralizing ability. This inability to neutralize hydrogen ions does not usually arise from a limited soil or mineral buffering capacity. Instead low cation exchange capacity and slow mineral dissolution rates in relation to the relatively short retention time of water within the soil system may result in incomplete neutralization of soil waters and acidification of surface waters (Driscoll, 1980). Characteristics of regions sensitive to surface water acidification are discussed in more detail in Section 7.4.1.

Sources of hydrogen ions to the edaphic-aquatic system include, besides acidic deposition, mechanisms for internal generation of hydrogen ion - oxidation reactions (e.g., pyrite oxidation, nitrification), cation uptake by vegetation (e.g., uptake of NH_4^+ or Ca^{++}), or generation of organic acids from incomplete organic litter decomposition (Figure 7-15). The relative importance of the hydrogen ion content in acidic deposition to the overall hydrogen ion budget of an ecosystem has been discussed by many researchers (Rosenqvist, 1976; SNSF Project, 1977).

The consensus is that changes in internal hydrogen ion generation related to land use or other changes (e.g., Drabløs and Sevaldrud, 1980) can not consistently account for the widespread acidification of surface waters occurring in southern Scandinavia, the Adirondack Region of New York, the LaCloche Mountain Area of Ontario, and elsewhere. Driscoll (1980) developed a hydrogen ion budget for the Hubbard Brook Area in New Hampshire. Based on these calculations, atmospheric hydrogen ion sources represent 48 percent of the total Hubbard Brook ecosystem hydrogen ion sources.

As noted above, fresh water ecosystems sensitive to inputs of acids are generally found in areas of poor soil development and underlain by highly siliceous types of bedrock resistant to dissolution through weathering (Likens et al., 1979). As a result, surface waters in such

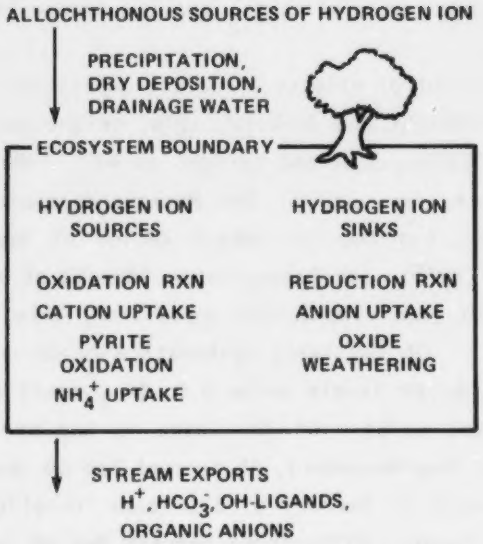

ALLOCHTHONOUS SOURCES OF HYDROGEN ION
PRECIPITATION,
DRY DEPOSITION,
DRAINAGE WATER
ECOSYSTEM BOUNDARY
HYDROGEN ION SOURCES
OXIDATION RXN
CATION UPTAKE
PYRITE OXIDATION
NH_4^+ UPTAKE
HYDROGEN ION SINKS
REDUCTION RXN
ANION UPTAKE
OXIDE WEATHERING
STREAM EXPORTS
H^+, HCO_3^-, OH-LIGANDS,
ORGANIC ANIONS

Figure 7-15. Schematic representation of the hydrogen ion cycle.

Source: Driscoll (1980).

areas typically contain very low concentrations of ions derived from weathering. The waters are diluted with low levels of dissolved salts and inorganic carbon, and low in acid neutralizing capacity. The chemical composition of acid lakes is summarized in Table 7-4 for lakes in southern Norway (Gjessing, et al., 1976), the west coast (Hörnstrom et al., 1976) and west-central regions of Sweden (Grahn, 1976), the LaCloche Mountains of southeastern Ontario (Beamish, 1976), and the vicinity of Sudbury, Ontario (Scheider et al., 1976), as well as for lakes not yet affected by acidification but in regions of similar geological substrata in west-central Norway (Gjessing et al., 1976) and the experimental lakes area of northwestern Ontario (Armstrong and Schindler, 1971). Basic cation concentrations (Ca, Mg, Na, K) are low (e.g., calcium levels of 18-450 μeq/liter or 0.4 - 9 mg/liter) relative to world-wide averages (15 mg/liter calcium, Livingstone, 1963). Bicarbonate is the predominant anion in most freshwaters (Stumm and Morgan, 1970). However, in acid lakes in regions affected by acidic deposition, sulfate replaces bicarbonate as the dominant anion (Wright and Gjessing, 1976; Beamish, 1976). With a decreasing pH level in acid lakes, the importance of the hydrogen ion to the total cation content increases.

Surveys to determine the extent of effects of acidic deposition on the chemistry of lakes have been conducted in Norway (Wright and Snekvik, 1978; Wright and Henriksen, 1978), Sweden (Almer et al., 1974; Dickson, 1975), Scotland (Wright et al., 1980a), the LaCloche Mountain area of Ontario (Beamish and Harvey, 1972), the Muskoka-Haliburton area of south-central Ontario (Dillon et al., 1978), and the Adirondack Region of New York State (Schofield, 1976a,b), Maine (Davis et al., 1978), and Pennsylvania (Arnold et al., 1980). In regions of similar geological substrata not receiving acidic deposition, lake pH levels average 5.6-6.7 (Armstrong and Schindler, 1971). Of 155 lakes systematically surveyed in southern Norway in October 1974, over 70 percent had pH levels below 6.0, 56 percent below 5.5, and 24 percent below 5.0 (Wright and Henriksen, 1978). Of 700 lakes in the Sørlandet Region of southern Norway surveyed in 1974 to 1975 (May-November), 65 percent had pH levels below 5.0 (Wright and Snekvik, 1978). On the west coast of Sweden, of 321 lakes investigated during 1968-1970, 93 percent had a pH level 5.5 or lower. Fifty-three percent had pH levels between 4.0 and 4.5 (Dickson, 1975). In the LaCloche Mountain Region of Ontario, 47 percent of 150 lakes sampled in 1971 had pH levels less than 5.5, and 22 percent had pH levels below 4.5 (Beamish and Harvey, 1972). In the Adirondacks, 52 percent of the high elevation (> 610 m) lakes had pH values below 5.0 (Schofield, 1976a,b). In each of these studies, the pH level of an individual lake could be related to, in most cases, the intensity of the acidic deposition and the geologic environment of the watershed. Atmospheric contributions of sea salts are also important in coastal regions.

Several methods have been developed to assess the degree of acidification in a lake and relate it to inputs of hydrogen ion or sulfate. Henriksen (1979) utilized alkalinity-calcium and pH-calcium relationships in lakes to estimate the degree of acidification experienced by a surface water. This technique is based on the premise that when carbonic acid weathering

TABLE 7-4. CHEMICAL COMPOSITION (MEAN ± STANDARD DEVIATION) OF ACID LAKES (pH <5) IN REGIONS RECEIVING HIGHLY ACIDIC PRECIPITATION (pH <4.5), AND OF SOFT-WATER LAKES IN AREAS NOT SUBJECT TO HIGHLY ACIDIC PRECIPITATION (pH >4.8)

Region		No. of lakes	Specific conductance††	μeq/l											Reference
				H (pH)	Na	K	Ca	Mg	HCO_3	HCl	SO_4	NO_3	Σ cations	Σ anions	
I. LAKES IN ACID AREAS															
Scandinavia															
Southernmost	Measured:	26	27±10	18±11 (4.76)	70±40	5±3	56±35	41±16	11±26	71± 45	100±33	4±2	189	186	Gjessing
Norway	Less s w*:			18	9	4	50	25	11	0	92	4	106	107	et al., 1976
Westcoast	Measured:	12	72**	43** (4.37**)	330	20	——— 280 ———		0	440	200	8	673	648	Hornström
Sweden	Less s w*:			43**	-50	13	-	-	0	0	155	8	-	-	et al., 1976
West-central	Measured:	6	47±23	22±15 (4.66)	165±120	15±8	75±10	80±40	-	170±90	200±70	19±4	360	390	Grahn
Sweden	Less s w*:			22	20	12	70	50	-	0	180	19	175	200	et al., 1976
North America															
La Cloche Mtns,	Measured:	4	38±8	20±9 (4.7)	26±4	10±3	150±25	75±8	0	22±6	290±40	-	280	310	Beamish,
Ontario	Less s w*:			20	9	10	150	65	0	0	290	-	255	290	1976
Sudbury,	Measured:	4	120±40	36±5 (4.5)	100±30	40±10	450±180	310±120	8±2	50±20†	800±290	-	940	850	Armstrong,
Ontario	Less s w*:			36	50	40	450	300	8	0	800	-	880	800	1971
II. LAKES IN UNAFFECTED AREAS															
Scandinavia															
West-central	Measured:	23	13±3	6±2 (5.2)	50±20	3±1	18±9	16±5	13±8	46±21	33±8	5±2	93	97	Gjessing
Norway	Less s w*:			6	9	3	16	7	13	0	30	5	41	48	et al., 1976
North America															
Experimental	Measured:	40	19	0.2-2 (5.6-6.7)	40	10	80	75	60	40	60	<1.5	200	160	Armstrong,
Lakes Area,	Less s w*:			0.2-2	4	10	80	65	60	0	55	<1.5	160	120	1971
Ontario															

*Less s w = Concentrations after subtracting the seawater contribution according to the procedure explained by Wright and Gjessing (1976).

**Data for 112 lakes

†Measured after past liming of the lakes

††μS/cm at 20°C

occurs one equivalent of alkalinity (acid neutralizing capacity) is released to the aquatic environment for every equivalent of basic cation (Ca, Mg, K, or Na) dissolved. On the other hand, if mineral acid weathering is occurring, for example as a result of acidic deposition, one equivalent of hydrogen ion is comsumed for every equivalent of cation solubilized. Therefore, for a given basic cation level, there is less aqueous acid neutralizing capacity in lakes in systems experiencing strong acid weathering than in systems experiencing carbonic acid weathering. When comparing alkalinity plots from two watersheds, one experiencing strong acid contributions and the other undergoing largely carbonic acid weathering (assuming both watersheds have similar edaphic environments), the difference in alkalinity between the two plots for a given calcium level (the dominant basic cation) should be indicative of the amount of strong acid the watershed receives and the degree of acidification of the surface water. For waters with pH levels below 5.6, alkalinity is approximately numerically equal to the hydrogen ion concentration with its sign changed. Therefore, pH level can be substituted for alkalinity, and pH-calcium plots developed (Figure 7-16). In the figure most of the lakes in northern and northwestern Norway fall below an empirically shown curve, whereas lakes in southernmost and southeastern Norway lie above this curve. Data of this type for Norway indicate that significant acidification of lakes has occurred in areas receiving precipitation with volume-weighted average concentrations of H^+ above 20-25 μeq/liter (pH 4.7-4.6) and sulfate concentrations above 1 mg/liter (20 μeq/liter) (Henriksen, 1979).

Henriksen (1979) also utilized the concentration of excess sulfate in lake water (sulfate in excess of that of marine origin) to estimate acidification. This suggests that bicarbonate anions lost in acidified lakes have been replaced by an equivalent amount of sulfate. Almer et al. (1978) plot pH levels in Swedish lakes as a function of excess sulfur load (excess sulfur in lake water multiplied by the yearly runoff) (Figure 7-17). Based on this relationship, they estimate that the most sensitive lakes in Sweden may resist a load of only about 0.3 g/m^2 of sulfur in lake water each year. At 1 g/m^2 of sulfur, the pH level of the lake will probably decrease below 5.0.

Elevated metal concentrations (e.g., aluminum, zinc, manganese, and/or iron) in surface waters are often associated with acidification (Schofield and Trojnar, 1980; Hutchinson et al., 1978; Wright and Gjessing, 1976; Beamish, 1976). Mobility of all these metals is increased at low pH values (Stumm and Morgan, 1970). For example, an inverse correlation between aluminum concentration and pH level has been identified for lakes in the Adirondack Region of New York State, southern Norway, the west coast of Sweden, and Scotland (Wright, 1980b) (Figure 7-18). Aluminum appears to be the primary element mobilized by strong acid inputs in precipitation and dry deposition (Cronan, 1978).

Aluminum is the third most abundant element by weight in the earth's crust (Foster, 1971). In general, aluminum is extremely insoluble and retained within the edaphic environment. However, with increased hydrogen ion inputs (via acidic deposition or other sources) into the

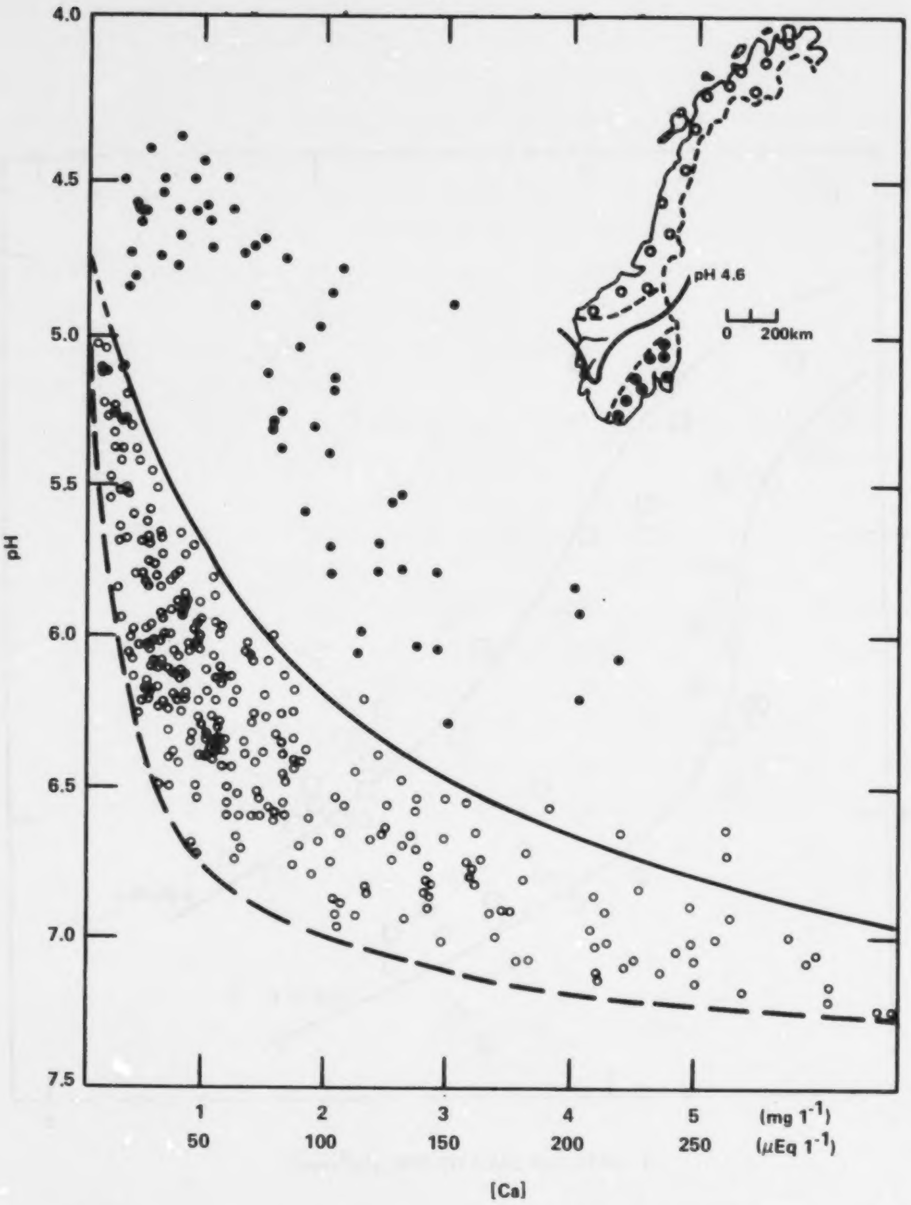


Figure 7-16. pH and calcium concentrations in lakes in northern and northwestern Norway sampled as part of the regional survey of 1975, in lakes in northwestern Norway sampled in 1977 (o) and in lakes in southernmost and southeastern Norway sampled in 1974 (●). Southern Norway receives highly acid precipitation (pH 4.2-4.5) and a large number of lakes have lost their fish populations due to high acidity. Inset shows areas in which these lakes are located. Areas south of isoline receive precipitation more acid than pH 4.6.

Source: Henriksen (1979).

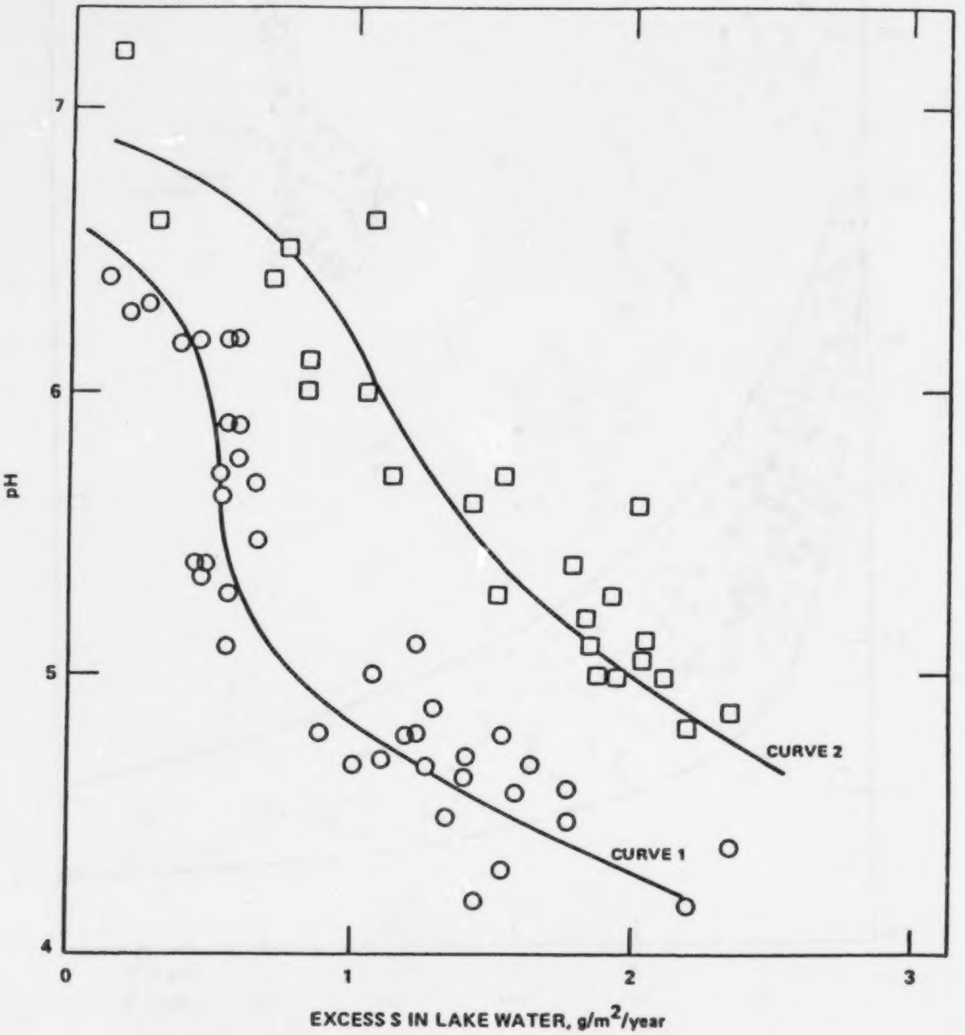


Figure 7-17. The pH value and sulfur loads in lake waters with extremely sensitive surroundings (curve 1) and with slightly less sensitive surroundings (curve 2). (Load = concentration of "excess" sulfur multiplied by the yearly runoff.)

Source: Almer et al. (1978).

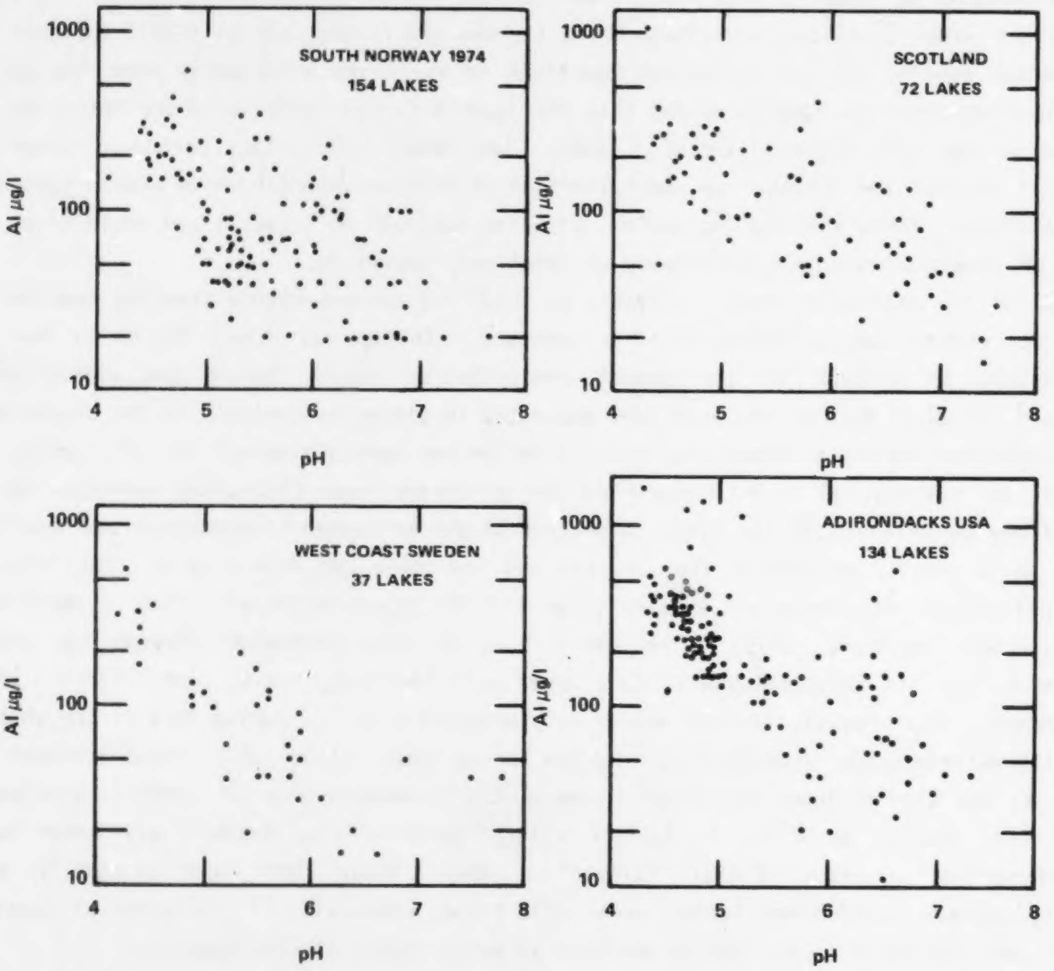


Figure 7-18. Total dissolved Al as a function of pH level in lakes in acidified areas in Europe and North America.

Source: Wright et al. (1980b).

edaphic environment, aluminum is rapidly mobilized. Cronan and Schofield (1979) suggest that input of strong acids may inhibit the historical trend of aluminum accumulation in the B soil horizon. Consequently, aluminum tends to be transported through the soil profile and into streams and lakes. Evidence from field data (Schofield and Trojnar, 1980) and laboratory experiments (Driscoll et al., 1979; Muniz and Leivestad, 1980) suggest that these elevated aluminum levels may be toxic to fish. Concentration of aluminum may be as important or more important than pH levels as a factor leading to declining fish populations in acidified lakes. Aluminum toxicity to aquatic biota other than fish has not been assessed.

Surface water chemistry, particularly in streams and rivers, may be highly variable with time. Since many of the neutralization reactions in soils are kinetically slow, the quality of the leachate from the edaphic system into the aquatic system varies with the retention time of water in the soil (Johnson et al., 1969). The longer the contact period of water with lower soil strata, the greater the neutralization of acid contribution from precipitation and dry deposition. Therefore, during periods of heavy rainfall or snowmelt and rapid water discharge, pH levels in receiving waters may be relatively depressed.

Many of the regions currently affected by acidification experience freezing temperatures during the winter and accumulation of a snowpack. In the Adirondack Region of New York approximately 55 percent of the annual precipitation occurs during the winter months (Schofield, 1976b). Much of the acid load deposited in winter accumulates in the snowpack and may be released during a relatively short time period during snowmelt in the spring. In addition, on melting, 50 to 80 percent of the pollutant load (including hydrogen ion and sulfate) may be released in the first 30 percent of the meltwater (Johannessen and Henriksen, 1978). As a result, melting of the snowpack and ice cover can result in a large influx of acidic pollutants into lakes and streams (Figure 7-19) (Gjessing et al., 1976; Schofield and Trojnar, 1980; Hultberg, 1976). The rapid flux of this meltwater through the edaphic environment, and its interaction with only upper soil horizons, limits neutralization of the acid content. As a result, surface waters only moderately acidic during most of the year may experience extreme drops in pH level during the spring thaw. Basic cation concentrations (Ca, Mg, Na, K) may also be lower during this time period (Johannessen et al., 1980). Similar but usually less drastic pH drops in surface waters (particularly streams) may occur during extended periods of heavy rainfall (Driscoll, 1980). These short term changes in water chemistry may have significant impacts on aquatic biota, especially if they occur at sensitive times in the life cycle (e.g., during spawning or early stages of development).

7.3.1.2 Effects on decomposition. The processing of dead organic matter (detritus) plays a central role in the energetics of lake and stream ecosystems (Wetzel, 1975). The organic matter may have been generated either internally (autochthonous) via photosynthesis within the aquatic ecosystem or produced outside the lake or stream (allochthonous) and later exported to the aquatic system. Detritus is an important food source for bacteria, fungi, some protozoa, and other animals. These organisms, through the utilization of detritus, release energy,

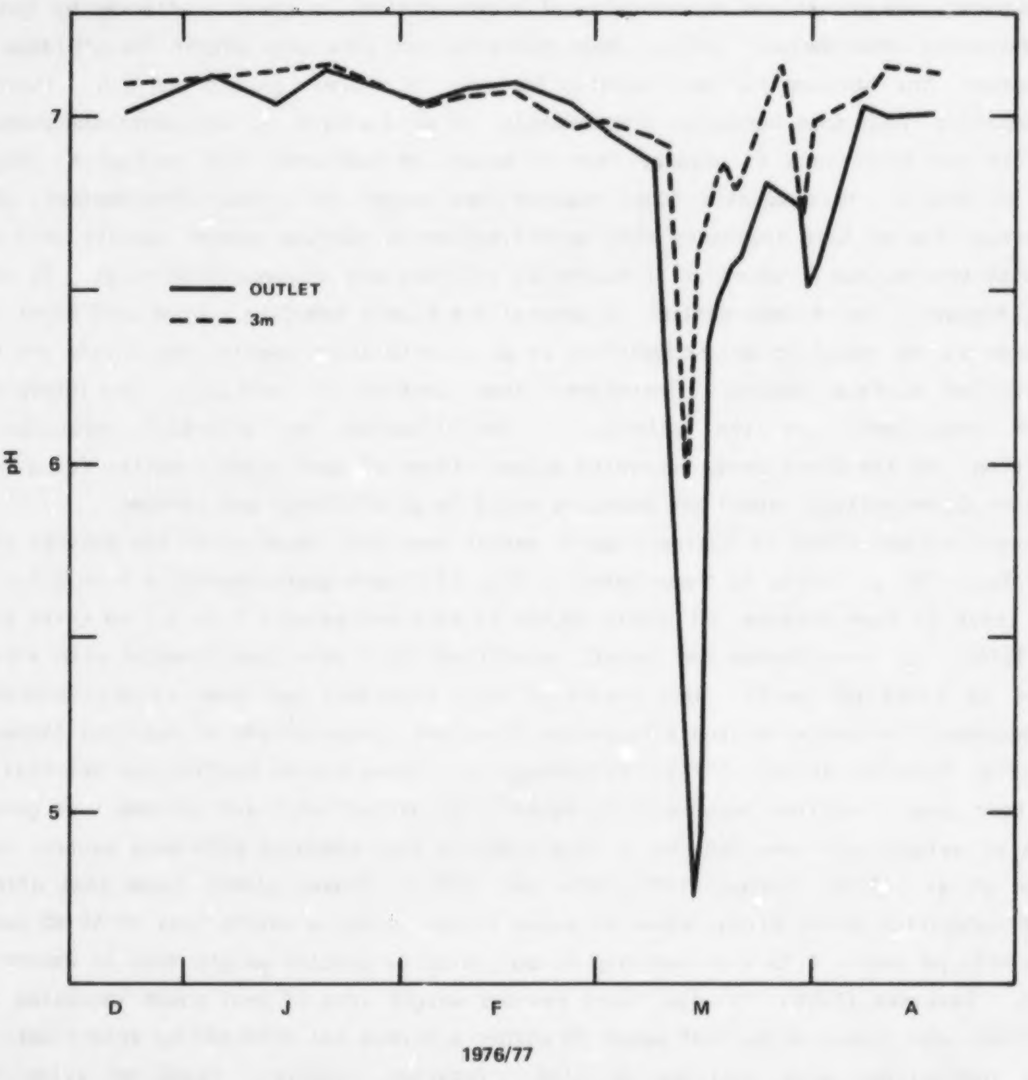


Figure 7-19. pH levels in Little Moose Lake, Adirondack region of New York State, at a depth of 3 meters and at the lake outlet.

Source: Adapted from Schofield and Trojnar (1980).

minerals and other compounds stored in the organic matter back into the environment. Initial processing of coarse particulate detritus is often accomplished by benthic invertebrate fauna. Among other things, the particles are physically broken down into smaller units, increasing their surface area. Biochemical transformations of particulate and dissolved organic matter occur via microbial metabolism and are fundamental to the dynamics of nutrient cycling and energy flux within the aquatic ecosystem.

In general, the growth and reproduction of microorganisms is greatly affected by hydrogen ion concentration (Rheinheimer, 1971). Many bacteria can grow only within the pH range of 4 to 9; however, the optimum for most aquatic bacteria is between pH 6.5 and 8.5. There are more acidophilic fungi than bacteria; consequently, in acid waters and sediments the proportion of fungi in the microflora is greater than in waters or sediments with neutral or slightly alkaline pH levels. Most aquatic fungi require free oxygen for growth (Rheinheimer, 1971).

Numerous studies have indicated that acidification of surface waters results in a shift in microbial species and a reduction in microbial activity and decomposition rates. It should be noted, however, that microorganisms in general are highly adaptive. With sufficient time, a given species may adapt to acid conditions or an acid-tolerant species may invade and colonize acidified surface waters. Therefore, some caution is necessary in interpreting short-term experiments on the effects of acidification on microbial activity and decomposition. On the other hand, increased accumulations of dead organic matter (as a result of decreased decomposition rates) are commonly noted in acidic lakes and streams.

Abnormal accumulations of coarse organic matter have been observed on the bottoms of six Swedish lakes. The pH levels in these lakes in July 1973 were approximately 4.4 to 5.4. Over the last three to four decades, pH levels appear to have decreased 1.4 to 1.7 pH units (Grahn et al., 1974). In both Sweden and Canada, acidified lakes have been treated with alkaline substances to raise pH levels. One result of this treatment has been an acceleration of organic decomposition processes and elimination of excess accumulations of detritus (Andersson et al., 1978; Scheider et al., 1975). Litterbags containing coarse particulate detrital matter have been used to monitor decomposition rates in acidified lakes and streams. In general, the rates of weight loss were reduced in acidic waters when compared with more neutral waters (Leivestad et al., 1976; Traaen, 1980; Petersen, 1980). Traaen (1980) found that after 12 months of incubation dried birch leaves or aspen sticks showed a weight loss of 50-80 percent in waters with pH levels 6 to 7 as compared to only a 30-50 percent weight loss in waters with pH 4 to 5. Petersen (1980) likewise found reduced weight loss of leaf packs incubated in an acidic stream when compared to leaf packs in either a stream not affected by acidification or a stream neutralized with addition of lime. Petersen, however, found no evidence of differences in microbial respiration between the streams. The acidic stream did show a reduction in the invertebrate functional group that specializes in processing large particles (shredders). Gahnstrom et al. (1980) found no significant differences in oxygen consumption by sediments from acidified and non-acidified lakes. Rates of glucose decomposition were also studied in lake sediment-water systems adapted to pH values from 3 to 9. Glucose transformation increased at pH levels above 6. Lime treatment of acidic Lake Högsjön in Sweden also increased rates of glucose processing. However in a humic lake, the maximum rate of glucose transformation occurred at the *in situ* value pH 5 (Gahnstrom et al., 1980)

Laboratory and field experiments involving decomposition rates have fairly consistently found decreasing microbial activity with increasing acidity. Traaen (1980) found that litter decomposition at pH level 5.2 was only 50 percent of that at pH 7.0 and at pH 3.5, only 30 percent that at pH 7.0. In addition, increasing acidity (pH 7.0 to 3.5) led to a shift from bacterial to fungal dominance. Incubations of profundal lake sediments at pH 4, 5, and 6 indicated a significant reduction in community respiration with increasing acidity, as well as a possible inhibition of nitrification and a lowering of sediment redox potentials. Bick and Drews (1973) studied the decomposition of peptone in the laboratory. With decreasing pH, total bacterial cell counts and numbers of species of ciliated protozoans decreased, decomposition and nitrification were reduced, and oxidation of ammonia ceased below pH 5. At pH 4 and lower, the number of fungi increased.

Disruption of the detrital trophic structure and the resultant interference with nutrient and energy cycling within the aquatic ecosystem may be one of the major consequences of acidification. Investigations into the effects of acidification on decomposition apparently have produced somewhat inconsistent results. However, many of these apparent inconsistencies arise only from a lack of complete understanding of the mechanisms relating acidity and rates of decomposition. It is fairly clear that in acidic lakes and streams unusually large accumulations of detritus occur, and these accumulations are related, directly or indirectly, to the low pH level. The processing of organic matter has been reduced. In addition, this accumulation of organic debris plus the development of extensive mats of filamentous algae on lake bottoms (discussed in Section 7.3.1.3) may effectively seal off the mineral sediments from interactions with the overlying water. As a result, regeneration of nutrient supplies to the water column is decreased both by reduced processing and mineralization of dead organic matter and by limiting sediment-water interactions. Primary productivity within the aquatic system may be substantially decreased as a result of this process (Section 7.3.1.3). These ideas have been formulated into the hypothesis of "self-accelerating oligotrophication" by Grahn et al. (1974).

7.3.1.3 Effect on primary producers and primary productivity. Organisms obtain their food (energy) directly or indirectly from solar energy. Sunlight, carbon dioxide, and water are used by primary producers (phytoplankton, other algae, mosses, and macrophytes) in the process of photosynthesis to form sugars which in turn are used by the plants or stored as starch. The stored energy may be used by the plants or pass through the food chain or web. Energy in any food chain or web passes through several trophic levels. Each link in the food chain is termed a trophic level. The major trophic levels are the primary producers, herbivores, carnivores, and the decomposers. Energy in an ecosystem moves primarily along two main pathways: the grazing food chain (primary producers-herbivores-carnivores) and the detrital food chain (Smith, 1980; Billings, 1978; Odum, 1971). Interactions between these two food chains are, however, extensive. Green plants convert solar energy to organic matter and, as such, are the base for both food chains. The grazing food chain involves primarily living organic matter; the detrital food chain, dead organic matter. Any changes as a result of acidification in the green plants and primary production within the aquatic ecosystem may therefore have a profound effect on all other organisms in the aquatic food web. As noted in Section 7.3.1.2, a portion of the detrital food chain is supported by dead organic matter imported into the aquatic system from external sources.

Extensive surveys of acidic lakes in Norway and Sweden (Leivestad et al., 1976; Almer et al., 1974) have observed changes in species composition and reduced diversity of phytoplankton correlated with decreasing lake pH level (Figure 7-20). Generally at normal pH values of 6 to 8, lakes in the west coast region of Sweden contain 30 to 80 species of phytoplankton per 100-ml sample in mid-August. Lakes with pH below 5 were found to have only about a dozen species. In some very acid lakes (pH<4), only three species were noted. The greatest changes in species composition occurred in the pH interval 5-6. The most striking change was the disappearance of many diatoms and blue-green algae. The families Chlorophyceae (green algae) and Chrysophyceae (golden-brown algae) also had greatly reduced numbers of species in acidic lakes (Figure 7-21). Dinoflagellates constituted the bulk of the phytoplankton biomass in the most acidic lakes (Almer et al., 1978). Similar phenomena were observed in a regional survey of 55 lakes in southern Norway (Leivestad et al., 1976) and in a study of nine lakes in Ontario (Stokes, 1980). Changes in species composition and reduced diversity have also been noted in communities of attached algae (periphyton) (Leivestad et al., 1976; Almer et al., 1978). Mougeotia, a green alga, often proliferates on substrates in acidic streams and lakes.

Shifts in the types and numbers of species present may or may not affect the total levels of primary productivity and algal biomass in acidic lakes. Species favored by acidic conditions may or may not have comparable photosynthetic efficiencies or desirability as a prey item for herbivores. On the other hand, decreased availability of nutrients in acidic water as a result of reduced rates of decomposition (Section 7.3.1.2) may decrease primary productivity regardless of algal species involved. In field surveys and experiments, relationships between pH level and total algal biomass and/or productivity were not as consistent as the relationship between pH and species diversity.

Kwiatkowski and Roff (1976) identified a significant linear relationship of decreasing chlorophyll a concentrations (indicative of algal biomass) with declining pH level in six lakes near Sudbury, Ontario, with a pH range of 4.05 to 7.15. In addition, primary productivity was reduced in the two most acid lakes (pH 4-4.6). Stokes (1980) also reports a decrease in total phytoplankton biomass with decreasing pH level for nine lakes in the same region of Ontario. Crisman et al. (1980) reported a linear decrease in functional chlorophyll measurements with declining pH for 11 lakes in northern Florida, pH range 4.5 to 6.9. On the other hand, Almer et al. (1978) note that in 58 nutrient-poor lakes in the Swedish west coast

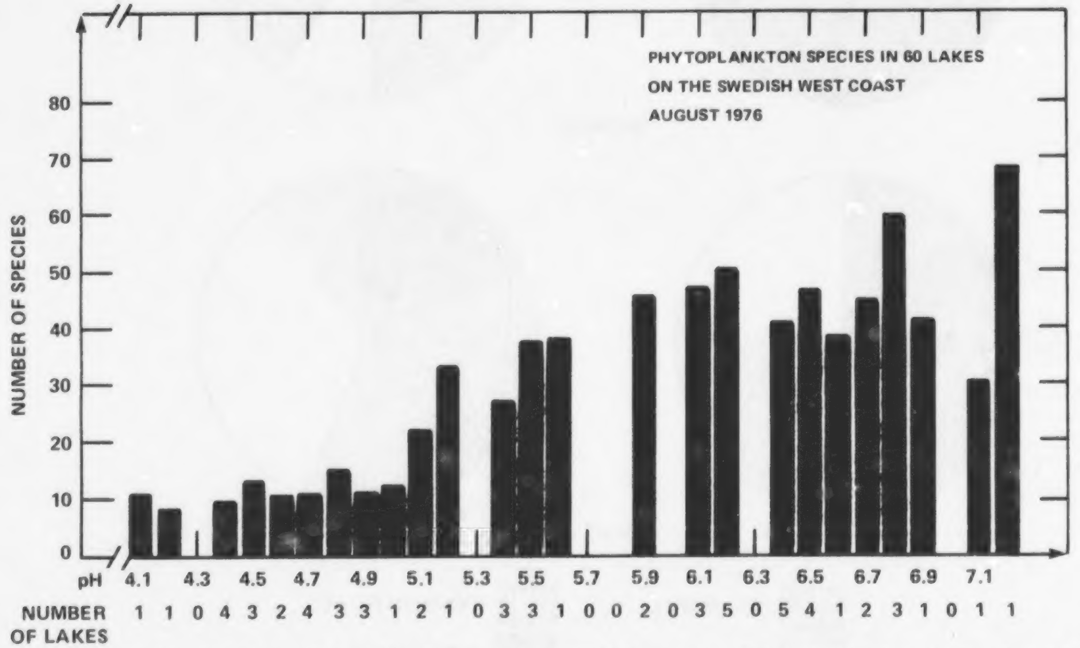


Figure 7-20. Numbers of phytoplankton species in 60 lakes having different pH values on the Swedish West Coast, August 1976.

Source: Adapted from Almer et al. (1978).

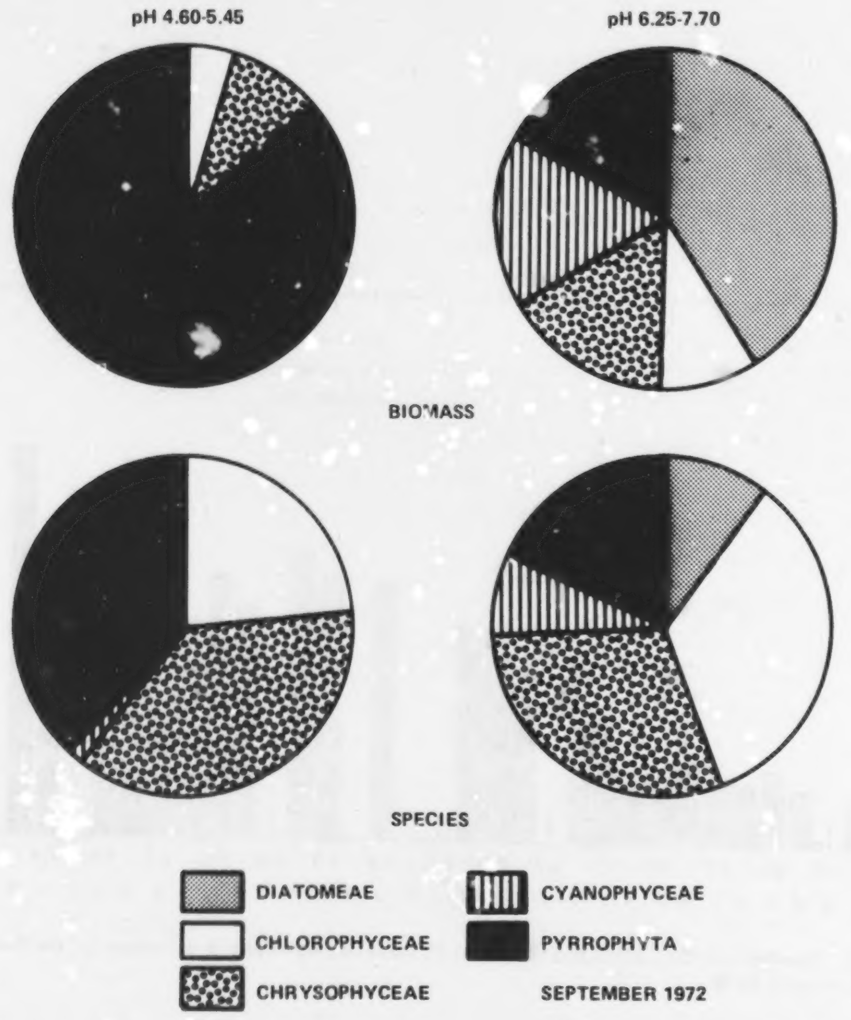


Figure 7-21. Percentage distribution of phytoplankton species and their biomasses. September 1972, west coast of Sweden. Biomass = living weight per unit area.

Source: Adapted from Almer et al. (1978).

region, the largest mean phytoplankton biomass occurred in the most acid lakes (pH <4.5). Yan and Stokes (1978) concluded that they have no evidence that the phytoplankton biomass in Carlyle Lake, with a summer pH level about 5.1, is below that observed in circumneutral lakes in the same region. In a continuing whole-lake acidification project (Schindler et al., 1980), a lowering of the epilimnion pH level from 6.7-7.0 in 1976 to 5.7-5.9 in 1978 resulted in no significant change in the chlorophyll concentration or primary production. Both in situ and experimental acidification have resulted in large increases in periphyton populations (Muller, 1980; Hendrey, 1976; Hall et al., 1980). Hendrey (1976) and Muller (1980) observed carbon uptake by periphyton incubated in vitro. They found that, although the total rate of photosynthesis increased with decreasing pH level due to the larger biomass at the lower pH, the photosynthesis per unit biomass decreased with pH.

From the above discussion it is obvious that not only is there no clear correlation between pH level and algal biomass or productivity, but the effects of acidification appear inconsistent between systems. Again, these apparent inconsistencies probably reflect a lack of knowledge about exact mechanisms relating acidification and lake metabolism, and also the complexity of these mechanisms and interactions. Changes in the algal community biomass and productivity probably reflect the balance between a number of potentially opposing factors: those that tend to decrease productivity and biomass versus those that tend to increase productivity and/or biomass when acidity increases. Factors working to decrease productivity and biomass with declining pH levels may include: (1) a shift in pH level below that optimal for algal growth; (2) decreased nutrient availability as a result of decreased decomposition rates and a sealing-off of the mineral sediments from the lake water; and (3) decreased nutrient availability as a result of changes in aquatic chemistry with acidification. For example, despite the fact that the optional pH range for growth of Tabellaria flocculosa is between 5.0 to 5.3 (Cholonky, 1968) or higher (Källqvist et al., 1975), this species dominated experimentally acidified stream communities at pH level 4 in three out of five replicates (Hendrey et al., 1980a). As noted in Section 7.3.1.1, aluminum concentrations increase with decreasing pH level in acidified lakes and streams. Aluminum is also a very effective precipitator of phosphorus, particularly in the pH range 5 to 6 (Dickson, 1978; Stumm and Morgan, 1970). In oligotrophic lakes, phosphorus is most commonly the limiting nutrient for primary productivity (Wetzel, 1975; Schindler, 1975). Therefore, chemical interactions between aluminum and phosphorus may result in a decreasing availability of phosphorus with decreasing pH level and, as a result, decreased primary production.

Factors working to increase productivity and/or biomass with acidification of a lake or stream may include: (1) decreased loss of algal biomass to herbivores; (2) increased lake transparency; and (3) increased nutrient availability resulting from nutrient enrichment of precipitation. Decreased population of invertebrates (as discussed in Section 7.3.1.4), particularly herbivorous invertebrates, may decrease grazing pressure on algae and result in unusual accumulations of biomass. Hendrey (1976) and Hall et al. (1980) include this mechanism as one hypothesis to explain their observation of increased biomass of periphyton at pH level 4 despite a decreased production rate per unit biomass.

Increases in lake transparency over time have been correlated with lake acidification in Sweden (Almer et al., 1978) and the Adirondack Region of New York (Schofield, 1976c). In addition, after the second year of experimental lake acidification (pH 6.7-7.0 to 5.7-5.9) in northwestern Ontario (Schindler et al., 1980), lake transparency increased by 1-2 m. These increases in transparency have not been correlated with decreases in phytoplankton biomass. Two mechanisms have been proposed. Aluminum acts as a very efficient precipitator for humic substances. Dickson (1978) found that humic substances are readily precipitated in the pH range 4.0 to 5.0. Dickson (1978) and Almer et al. (1978) suggest that increases in aluminum levels with lake acidification (Section 7.3.1.1) have resulted in increased precipitation of humics from the water column and therefore increased lake transparency. Almer at al. (1978) provide data for one lake on the west coast of Sweden. The pH level declined from above 6 to about 4.5 between 1940 and 1975. The secchi disc reading (Depth at which 9-inch disc is visible to the naked eye when lowered into the water) increased from about 3m to about 10m over the same period. Organic matter in the water (as estimated by $KMnO_4$ demand) decreased from 24 to 8 mg/liter from 1958 to 1973. Schindler et al. (1980), on the other hand, found no change in levels of dissolved organic carbon with acidification. Instead, changes in hydrolysis of organic matter with declining pH level may affect the light absorbancy characteristics of the molecules. Levels of particulate organic carbon, and changes with pH level, were not reported by Schindler et al. (1980).

Acidification of precipitation (and dry deposition) has been accompanied by increases in levels of sulfate and nitrate. Both of these are nutrients required by plants. However, as noted above, the primary nutrient limiting primary productivity in most oligotrophic lakes is phosphorus. Almer et al. (1978) report that atmospheric deposition rates of phosphorus have also increased in recent years. The world-wide extent of the correlation between acidic deposition and increased atmospheric phosphorus loading, however, is not known. It is expected that changes in atmospheric phosphorus loading would be much more localized than changes in acidic deposition. It is possible that in some areas increased atmospheric loading of phosphorus has occurred in recent years coincidentally with increased acidic deposition. Increased phosphorus nutrient loading into lakes may then increase primary production rates.

The effect of acidification on primary productivity and algal biomass of a particular stream or lake system depends upon the balance of the above forces. Differences in the importance of these factors between systems may account for inconsistencies in the response of different aquatic systems to acidic deposition. Acidification does, however, result in a definite change in the nutrient and energy flux of the aquatic system, and this change may eventually limit the total system biomass and productivity.

Acidification of lakes has also been correlated with changes in the macrophyte community. Documentation for these changes comes mainly from lakes in Sweden. Grahn (1976) reported that in five of six lakes studied during the last three to five decades, the macrophyte communities dominated by Lobelia and Isoetes have regressed whereas communities dominated by Sphagnum mosses have expanded. Acidity levels in these lakes apparently have increased, as indicated by a drop of approximately 1.3 to 1.7 pH units since the 1930's to 1940's. In acid lakes where conditions are suitable the Sphagnum peat moss may cover more than 50 percent of the bottom above the 4-m depth, and may also grow at much lower depths (Almer et al., 1978). The Sphagnum invasion may start at lake pH levels just below 6 (Almer et al., 1978). Similar growths of Sphagnum occur in Norwegian lakes (Galloway, 1978). Increases in Sphagnum as a benthic macrophyte have been documented from one lake in the Adirondack Region of New York (Hendrey and Vertucci, 1980).

Under acid conditions the Sphagnum moss appears to simply outgrow flowering plant aquatic macrophytes. In laboratory tests, the growth and productivity of the rooted macrophyte Lobelia was reduced by 75 percent at a pH of 4, compared with the control (pH 4.3-5.5). The period of flowering was delayed by ten days at the low pH (Laake, 1976). At low pH levels ($pH<5$), essentially all the available inorganic carbon is in the form of carbon dioxide or carbonic acid (Stumm and Morgan, 1970). As a result, conditions may be more favorable for Sphagnum, an acidophile that is not able to utilize the carbonate ion.

Besides the shift in macrophyte species, the invasion of Sphagnum into acid lakes may have four other impacts on the aquatic ecosystem. Sphagnum has a very high ion-exchange capacity, withdrawing basic cations such as Ca^{++} from solution and releasing H^+(Anschütz and Gessner, 1954; Almer et al., 1978). As a result, the presence of Sphagnum may intensify the acidification of the system and decrease the availability of basic cations for other biota. Second, dense growths of Sphagnum form a biotype that is an unsuitable substratum for many benthic invertebrates (Grahn, 1976). Growths of Sphagnum in acidic lakes are also often associated with felts of white mosses (benthic filamentous algae) and accumulations of nondecomposed organic matter. In combination, these organisms and organic matter may form a very effective seal. Interactions between the water column and the mineral sediments, and the potential for recycling of nutrients from the sediments back into the water body, may be reduced (Grahn, 1976; Grahn, et al., 1974). These soft bottoms may also be colonized by other macrophytes. In Sweden, Almer et al. (1978) report that growths of Juncus, Sparaganium, Utricularia, Nuphar, and/or Nymphaea, in addition to Sphagnum, may be extensive in acidic lakes. Thus primary production by macrophytes in lakes with suitable bottoms may be very large. Increased lake transparency may also increase benthic macrophyte and algal primary productivity.

7.3.1.4 Effects on invertebrates--In regional surveys conducted in southern Norway (Hendrey and Wright, 1976), the west coast of Sweden (Almer et al., 1978), the LaCloche Mountain Region of Canada (Sprules, 1975), and near Sudbury, Ontario (Roff and Kwiatkowski, 1977) numbers of species of zooplankton were strongly correlated with pH level (Figure 7-22). Changes in community structure were most noticeable at pH levels below 5. Certain species (e.g., of the

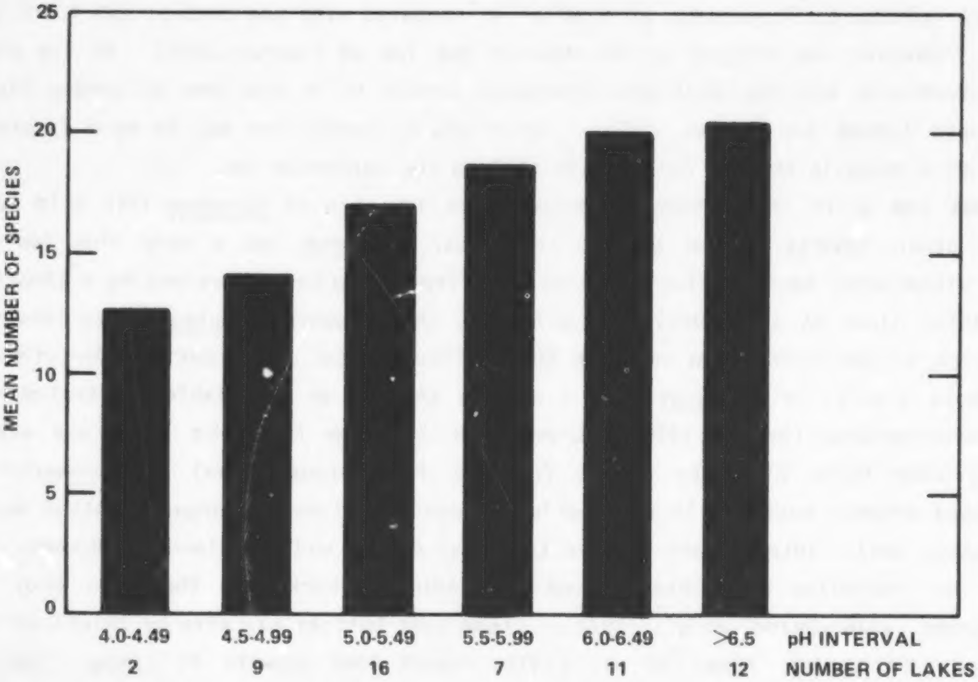


Figure 7-22. The number of species of crustacean zooplankton observed in 57 lakes during a synoptic survey of lakes in southern Norway. Source: Hendry et al (1976).

genera *Bosmina*, *Cyclops*, *Diaptomus*, as well as rotiferans, of the genera *Polyarthra*, *Keratella*, and *Kellicottia*) apparently have a high tolerance of acidic conditions and were commonly found in the pH interval 4.4 to 7.9. Others, such as cladocerans of the *Daphnia* genus, apparently are more sensitive and were only rarely found at pH <6 (Almer et al., 1978).

Similar studies of the relationship between pH level and biomass or productivity of zooplankton are not available. Proposed mechanisms for interactions between lake acidification and zooplankton populations are therefore largely hypothetical.

The species, population size, and productivity of zooplankton are affected both by changes in the quality and quantity of the food supply and shifts in predator populations. Changes in zooplankton species and production in response to changes in fish populations have been clearly demonstrated (Brooks and Dodson, 1965; Walters and Vincent, 1973; Dodson, 1974). Elimination of fish predators often results in dominance of the zooplankton community by large-bodied species. Absence of invertebrate predators (e.g., large-bodied carnivorous zooplankton) as a result of fish predation or other reasons often results in the prevalence of small-bodied species (Lynch, 1979). Surveys of acidic lake waters often have shown the dominance of small-bodied herbivores in the zooplankton community (Hendrey et al, 1980a). Fish also often are absent at these pH levels (Section 7.3.1.5). Different zooplankton species may have different physiological tolerances to depressed pH levels (e.g., Potts and Fryer, 1979). Food supplies, feeding habits, and grazing of zooplankton may also be altered with acidification as a consequence of changes in phytoplankton species composition and/or decreases in biomass or productivity of phytoplankton. Zooplankton also rely on bacteria and detrital organic matter for part of their food supply. Thus an inhibition of the microbiota or a reduction in microbial decomposition (Section 7.3.1.2) may also affect zooplankton populations. These alternate mechanisms postulated to underlie changes in community structure and/or production of zooplankton communities probably play an important role in zooplankton responses to acidification.

Synoptic and intensive studies of lakes and streams also have demonstrated that numbers of species of benthic invertebrates are reduced along a gradient of decreasing pH level (Sutcliffe and Carrick, 1973; Leivestad et al., 1976; Conroy et al., 1976; Almer et al., 1978; Roff and Kwiatkowski, 1977). In 1500 freshwater localities in Norway studied from 1953-73, snails were generally present only in lakes with pH levels above 6 (Okland, J., 1980). Likewise *Gammarus Lacustris*, a freshwater shrimp and an important element in the diet of trout in the Norwegian lakes where it occurs, was not found at pH levels below 6.0 (Økland, K., 1980, J. and K. Økland, 1980). Experimental investigations have shown that adults of this species cannot tolerate two days of exposure to pH 5.0 (Leivestad et al., 1976). Eggs were reared at six different pH levels (4.0 to 6.8). At a pH of 4.5, a majority of the embryos died within 24 hours. Thus, the short-term acidification which often occurs during the spring melt of snow could eliminate this species from small lakes (Leivestad et al., 1976). Fiance (1977) concluded that ephemeropterans (mayflies) were particularly sensitive to low pH levels and their populations were reduced in headwater streams of the Hubbard Brook watershed in New Hampshire. In laboratory studies, Bell (1971), Bell and Nebecker (1969), and Raddum (1978) measured the tolerance of some stream macroinvertebrates to low pH levels. Tolerance seems to be in the order caddisflies > (more tolerant than) stoneflies > mayflies (Hendrey et al., 1980).

Leivestad et al. (1976) reported on decreased standing crops (numbers/m^2 and g/m^2) of benthic invertebrates in two lakes with pH levels near 4.5 as compared to five lakes with pH near 6.0. Chironamids were the dominant group in all lakes. No fish were found in the acid lakes. Lack of predation by fish should favor increases in benthic biomass, the opposite of that observed. On the other hand, Hendrey et al. (1980a), based on data from eight Ontario lakes (pH 4.3 - < 5.7), reported no reduction in abundance of benthos related to pH level.

Air-breathing aquatic insects (e.g., backswimmers, water boatmen, and water striders) appear to be very tolerant of acidic environments. Population densities are often greater in acidic lakes and in the most acid lakes than in circumneutral lakes. Abundance of these large invertebrates may be related to reduced fish predation (Hendrey et al., 1980a).

Hall et al. (1980) experimentally acidified a stream to pH 4 and monitored reactions of macroinvertebrate populations. Initially following acidification, there was a 13-fold increase in downstream drift of insect larvae. Organisms in the collector and scraper functional groups were affected more than predators. Benthic samples from the acidified zone of Norris Brook contained 75 percent fewer individuals than those for reference areas. There was also a 37 percent reduction in insect emergence; members of the collector group were most affected. Insects seem to be particularly sensitive at emergence (Bell, 1971). Many species of aquatic insects emerge early in the spring through cracks in the ice and snow cover. These early-emerging insects therefore are exposed in many cases to the extremely acidic conditions associated with snowmelt (Hagen and Langeland, 1973).

Low pH also appeared to prevent permanent colonization by a number of invertebrate species, primarily herbivores, in acidified reaches of River Dudden, England (Sutcliffe and Carrick, 1973). Ephemeroptera, trichoptera, Ancylus (Gastropoda) and Gammarus were absent in these reaches.

Damage to invertebrate communities may influence other components of the food chain. Observations that herbivorous invertebrates are especially reduced in acidic streams, as reported in Norris Brook and River Dudden, support the hypothesis (Hendrey, 1976; Hall et al., 1980a) that changes in invertebrate populations may be responsible for increased periphytic algal accumulations in acidic streams and benthic regions of acidic lakes (Hendrey et al., 1980). Benthic invertebrates also assist with the essential function of processing dead organic matter. Petersen (1980) noted that decomposition of coarse particulate organic matter in leaf packs was lower in an acidic stream than in two streams with circumneutral pH levels. The invertebrate community also showed a reduction in the invertebrate functional group that specializes in processing large particles (shredders). In unstressed aquatic ecosystems, a continuous emergence of different insect species is available to predators from spring to autumn. In acid-stressed lakes or streams, the variety and numbers of prey may be reduced. Periods may be expected to occur in which the amount of prey available to fish (or other predators) is diminished.

7.3.1.5 Effects on fish--Acidification of surface waters has had its most obvious, and perhaps the most severe, impact on fish populations. Increasing acidity has resulted not just in changes in species composition or decreases in biomass but, in many cases, in total elimination of populations of fish from a given lake or stream. Extensive depletion of fish stocks has occurred in large regions of Norway, Sweden, and parts of eastern North America. Both commercial and sport fisheries have been affected in these areas. However, precise assessments of losses--in terms of population extinctions, reductions in yields, or economic and social impacts--either have not been attempted or are still in the process of evaluation. Potential damage to fish populations inhabiting other acid-sensitive aquatic ecosystems in New England, the Appalachians, and parts of Southeastern, North central, and Northwestern United States have not yet been assessed (Galloway, 1978).

Declines in fish populations have been related to acidification of surface waters in the Adirondack Region of New York State (Schofield 1976c), southern Norway (Jensen and Snekvik, 1972; Wright and Snekvik, 1978), southwestern Sweden (Almer et al., 1974), the LaCloche Mountain Region in southern Ontario (Beamish and Harvey, 1972), and southwestern Scotland (Wright et al., 1980a). Schofield (1976c) estimated that in 1975 fish populations in 75 percent of Adirondack lakes at high elevation (<610 m) had been adversely affected by acidification. Fifty-one percent of the lakes had pH values less than 5, and 90 percent of these lakes were devoid of fish life (Figure 7-23). Comparable data for the period 1929 to 1937 indicated that during that time only about 4 percent of these lakes had pH values below 5 and were devoid of fish (Figure 7-24). Therefore, entire fish communities consisting of brook trout (Salvelinus fontinalis), lake trout (Salvelinus namaycush), white sucker (Catostomus commersoni), brown bullhead (Icaturus nebulosus), and several cyprinid species were apparently eliminated over a period of 40 years. This decrease in fish populations was associated with a decline in lake pH level. A survey of more than 2000 lakes in southern Norway, begun in 1971, found that about one third of these lakes had lost their fish population (primarily brown trout, Salmo trutta L.) since the 1940's (Wright and Snekvik, 1978). Fish population status was inversely related to lake acidity (Leivestad et al., 1976). Declines in salmon populations in southern Norwegian rivers were reported as early as the 1920's. The catch of Atlantic salmon (Salmo salar, L.) in seven acidified southern Norwegian rivers is now virtually zero (Figure 7-25). In northern and western rivers not affected by acidification, no distinct downward trend in catch has occurred (Leivestad et al., 1976; Wright et al., 1976; Jensen and Snekvik, 1972). Similar changes have been observed in Sweden (Almer et al., 1974) where it is estimated that 10,000 lakes have been acidified to a pH less than 6.0 and 5,000 below a pH of 5.0 (Dickson, 1975). Populations of lake trout, lake herring (Coregonus artedii), white suckers, and other species disappeared rapidly during the 1960's from a group of remote lakes in the LaCloche Mountain Region of Ontario (Beamish et al., 1975).

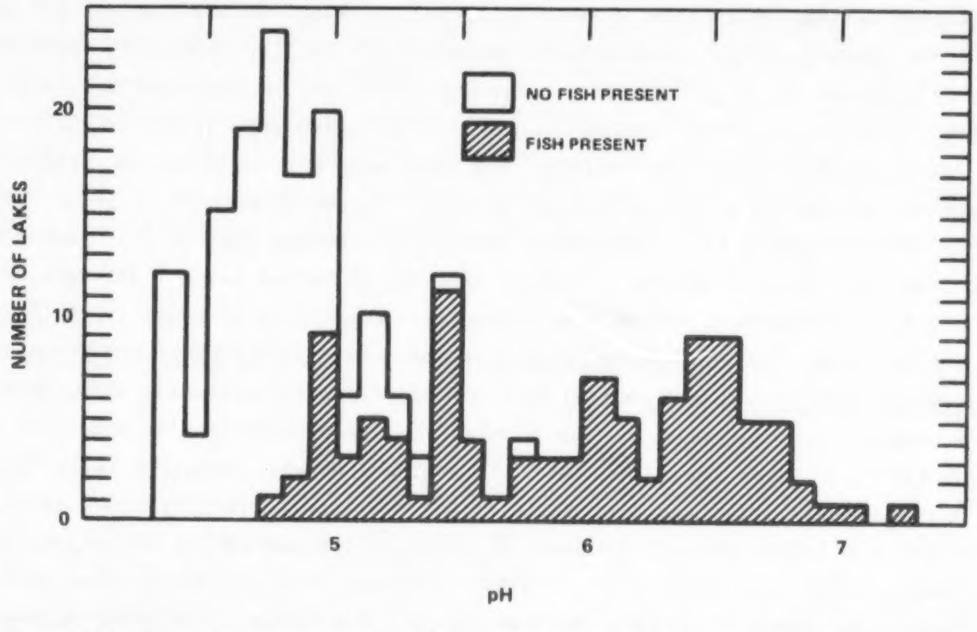


Figure 7-23. Frequency distribution of pH and fish population status in Adirondack Mountain lakes greater than 610 meters elevation. Fish population status determined by survey gill netting during the summer of 1975.

Source: Schofield (1976b).

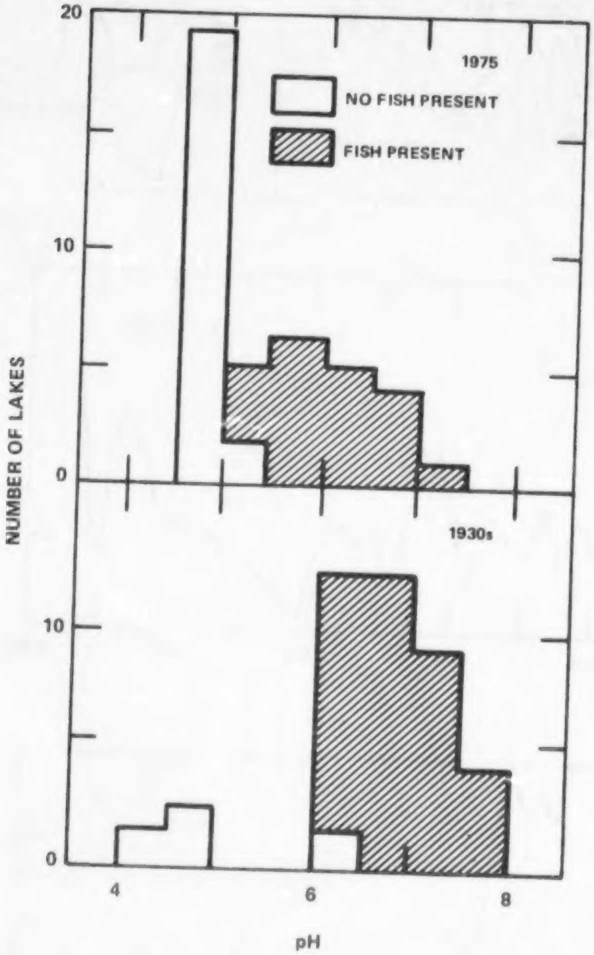


Figure 7-24. Frequency distribution of pH and fish population status in 40 Adirondack lakes greater than 610 meters elevation, surveyed during the period 1929-1937 and again in 1975.

Source: Schofield (1976 b).

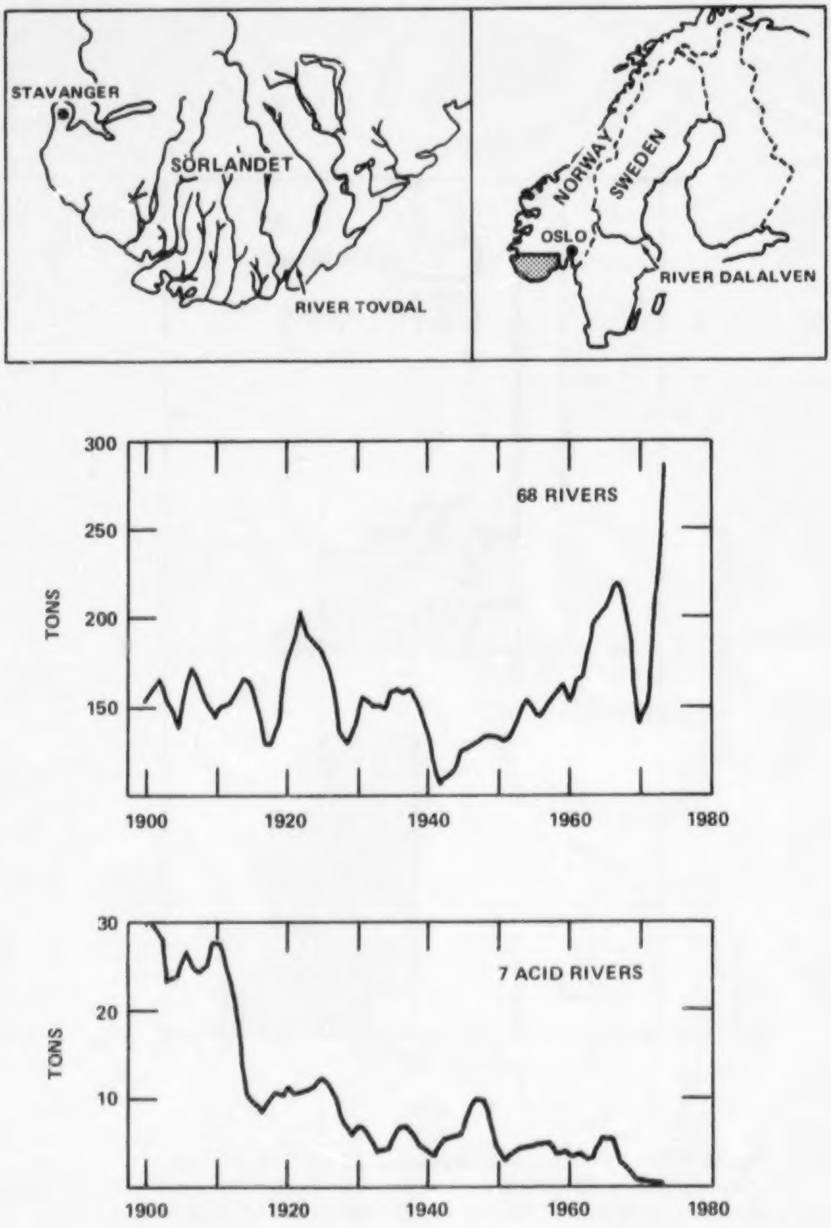


Figure 7-25. Norwegian salmon fishery statistics for 68 unacidified and 7 acidified rivers.

Source: Adapted from Almer et al. (1978).

It is difficult to determine at what pH level fish species disappear from lakes. Disappearance of the fish is usually not due to massive fish kills, but is the result of a gradual depletion of the population following reproductive failures (Leivestad et al., 1976). Field surveys in Scandinavia and eastern North America (Wright and Snekvik, 1978; Almer et al., 1974; Schofield, 1976c) suggest that many species do not occur in lakes with pH values below 5.0.

However, large spatial and temporal fluctuations in pH, and the possibility for "refuge areas" from acidic conditions during critical periods make it extremely difficult to generalize about effects of acidification on fish populations based on grab samples or annual mean pH levels. The pH levels identified in the literature as critical for reproduction of a species or correlated with the absence of a species in lake surveys are summarized in Table 7-5. Values range from pH 4.4 to over 6.0, and are highly species dependent.

TABLE 7-5. pH LEVELS IDENTIFIED IN FIELD SURVEYS AS CRITICAL TO LONG-TERM SURVIVAL OF FISH POPULATIONS

Family	Species	Critical pH	Reference
Salmonidae	Brook trout (*Salvelinus fontinalis*)	5.0	Schofield, 1976c
	Lake trout (*Salvelinus namaycush*)	5.1 5.2-5.5	Schofield, 1976c Beamish, 1976
	Brown trout (*Salmo trutta*)	5.0	Almer et al., 1978
	Arctic char (*Salvelinus alpinus*)	5.2	Almer et al., 1978
Percidae	Perch (*Perca fluviatilis*)	4.4-4.9	Almer et al., 1978
	Yellow perch (*Perca flavescens*)	4.5-4.7	Beamish, 1976
	Walleye (*Stigostedion vitreum*)	5.5-6.0+	Beamish, 1976
Catostomidae	White sucker (*Catostomus commersoni*)	4.7-5.2 5.1	Beamish, 1976 Schofield, 1976c
Ictaluridae	Brown bullhead (*Icaturus nebulosus*)	4.7-5.2 5.0	Beamish, 1976 Schofield, 1976c
Cyprinidae	Minnow (*Phoxinus phoxinus*)	5.5	Almer et al., 1978
	Roach (*Rutilus rutilus*)	5.5	Almer et al., 1978
	Lake chub (*Couesius plumbeus*)	4.5-4.7	Beamish, 1976
	Creekchub (*Semotilus atromaculatus*)	5.0	Schofield, 1976c
	Commonshiner (*Notropis cornutas*)	5.5	Schofield, 1976c
	Goldenshiner (*Notemigonus crysoleucas*)	4.9	Schofield, 1976c
Centrarchidae	Smallmouth bass (*Micropterus dolomieui*)	5.5-6.0+	Beamish, 1976
	Rock bass (*Ambloplites rupestris*)	4.7-5.2	Beamish, 1976
Esocidae	Pike (*Esox lucius*)	4.4-4.9	Almer et al., 1978

Recent field and laboratory studies (Schofield and Trojnar, 1980; Dickson, 1978; Driscoll et al., 1979; Baker and Schofield, 1980; Muniz and Leivestad, 1980) have indicated that aluminum levels in acidic surface waters (Section 7.3.1.1, Figure 7-18) may be highly toxic to fish (and perhaps other biota). Schofield and Trojnar (1980) analyzed survival of brook trout stocked into 53 Adirondack lakes as a function of 12 water quality parameters. Levels of pH, calcium, magnesium, and aluminum were significantly different between the two groups of lakes, with and without trout survival. However, after accounting for the effects of aluminum concentrations on differences between the two groups of lakes, differences in calcium, magnesium, and pH levels were no longer significant. Aluminum, therefore, appears to be the primary chemical factor controlling survival of trout in these lakes. Likewise, in laboratory experiments with natural Adirondack waters and synthetic acidified aluminum solutions, levels of aluminum, and not the pH level per se, determined survival and growth of fry of brook trout and white suckers (Baker and Schofield, 1980). In addition, speciation of aluminum had a substantial effect on aluminum toxicity. Complexation of aluminum with organic chelates eliminated aluminum toxicity to fry (Baker and Schofield, 1980; Driscoll et al., 1979). As a result, waters high in organic carbon, e.g., acidic bog lakes, may be less toxic to fish than surface waters at similar pH levels but with lower levels of dissolved organic carbon.

Inorganic aluminum levels, and not low pH levels, may therefore be a primary factor leading to declining fish populations in acidified lakes and streams. However, many laboratory or in situ field experiments have been conducted on the effects of pH on fish without taking into account aluminum or other metal concentrations in naturally acidic waters. As a result, many of the conclusions based on these experiments regarding pH levels critical for fish survival are suspect. Therefore these experiments will not be reviewed here.

Sensitivity of fish and other biota to low pH levels has also been shown to depend on aqueous calcium levels (Wright and Snekvik, 1978; Trojnar, 1977a,b; Bua and Snekvik, 1972). In southern Norway, the mean calcium level in lakes studied was approximately 1.1 mg/liter, as compared to about 3 mg/liter in the LaCloche Mountain Region (Table 7-4) or 2.1 mg/liter in the Adirondack Region (Schofield, 1976b). In Norwegian lakes, Wright and Snekvik (1978) identified pH and calcium levels as the two most important chemical parameters related to fish status.

Decreased recruitment of young fish has been cited as the primary factor leading to the gradual extinction of fish populations (Leivestad et al., 1976; Rosseland et al., 1980; Wright and Snekvik, 1978). Field observations (Jensen and Snekvik, 1972; Beamish, 1974; Schofield, 1976a; Almer et al., 1974) indicate changes in population structure over time with acidification. Declining fish populations consist primarily of older and larger fish with a decrease in total population density. Recruitment failure may result from inhibition of adult fish spawning and/or increased mortality of eggs and larvae. Effects on spawning and decreased egg deposition may be associated with disrupted spawning behavior and/or effects of acidification on reproductive physiology in maturing adults (Lockhart and Lutz, 1976). Field observations by Beamish et al. (1975) related reproductive failure in white suckers to an inability of females to release their eggs. On the other hand, Amundsen and Lunder (1974) observed total mortality of naturally spawned trout eggs in an acid brook a few weeks after spawning. A summary of Norwegian studies (Leivestad et al., 1976) concluded that egg and fry mortality is the main cause of fish reproduction failure. Spawning periods and early life history stages for many fish species coincide with periods of extreme acidity, particularly during and immediately after snowmelt in the spring.

In some lakes, fish population decreases are associated with a lack of older fish (Rosseland et al., 1980). In Lake Tveitvatn on the Tovdal River in southern Norway, brown trout mortality apparently occurs primarily after the first spawning. Since 1976, no fish past spawning age have been found, and population density has decreased steadily (Rosseland et al., 1980). Fish kills of adult salmon in rivers in southern Norway were recorded as early as 1911 (Leivestad et al., 1976).

When evaluating the potential effects of acidification on fish or other biotic populations, it is very important to keep in mind the highly diversified nature of aquatic systems spatially, seasonally, and year-to-year. As a result of this diversity, it is necessary to evaluate each system independently in assessing the reaction of the population to acidification. Survival of a fish population may depend more on the availability of refuge areas from acid conditions during spring melt or of one tributary predominantly fed by baseflow (fed from the bottom) and supplying an adequate area for spawning, than on mean annual pH, calcium, or inorganic aluminum levels.

7.3.1.6 *Effects on vertebrates other than fish*. Certain species of amphibians may be the vertebrate animals, other than fish, most immediately and directly affected by acidic deposition (Pough and Wilson, 1976). Their vulnerability is due to their reproductive habits. In temperate regions, most species of frogs and toads, and approximately half of the terrestrial salamanders, lay eggs in ponds. Many of these species breed in temporary pools formed each year by accumulation of rain and melted snow. Approximately 50 percent of the species of toads and frogs in the United States regularly breed in ephemeral pools; about one-third of the salamander species that have aquatic eggs and larvae and terrestrial adults breed in temporary pools. Most of these pools are small and collect drainage from a limited area. As a result, the acidity of the eater in these pools is strongly influenced by the pH of the precipitation that fills them. Ephemeral pools are usually more acidic than adjacent permanent bodies of water. Pough and Wilson (1976) report that in 1975, in the vicinity of Ithaca, N.Y., the average pH of 12 temporary ponds was 4.5 (range 3.5 to 7.0), while the average pH of six permanent ponds was 6.1 (range 5.5 to 7.0). Amphibian eggs and larvae in temporary pools are exposed to these acidic conditions.

Pough and Wilson (1976) and Pough (1976) studied the effect of pH level on embryonic development of two common species of salamanders, the spotted salamander (*Ambystoma maculatum*) and the Jefferson salamander (*A. jeffersonianum*). In laboratory experiments, embryos of the spotted salamander tolerated pH levels from 6 to 10 but had greatest hatching success at pH 7 to 9. The Jefferson salamander tolerated pH levels 4 to 8 and was most successful at 5 to 6. Mortality of embryos rose abruptly beyond the tolerance limits. In a four-year study of a large breeding pond (pH 5.0-6.5), 938 adult spotted salamanders produced 486 metamorphosed juveniles (0.52 juveniles/adult), while 686 adult Jefferson salamanders produced 2157 juvenile (3.14 juveniles/adult). Based on these findings, Pough and Wilson (1976) predict that continued acidic deposition may result in substantial shift in salamander and other amphibian populations. Gosner and Black (1957) report that only acid-tolerant species of amphibians can breed in the acid (pH 3.6 to 5.2) sphagnaceous bogs in the New Jersey Pine Barrens.

Frog populations in Tranevatten, a lake near Gothenberg, Sweden, acidified by acidic precipitation, have also been investigated (Hagström, 1977; Hendrey, 1978). The lake has pH levels ranging from 4.0 to 4.5. All fish have disappeared, and frogs belonging to the species Rana temporaria and Bufo bufo are being eliminated. At the time of the study (1977) only adult frogs eight to ten years old were found. Many egg masses of Rana temporaria were observed in 1974, but few were found in 1977, and the few larvae (tadpoles) observed at that time died.

Frogs and salamanders are important predators on invertebrates, such as mosquitoes and other pest species, in pools, puddles, and lakes. They also are themselves important prey for higher trophic levels in an ecosystem. In some habitats, salamanders are the most abundant vertebrates. In a New Hampshire forest, for example, salamanders were found to exceed birds and mammals in both numbers and biomass (Hanken et al., 1980).

The elimination of fish and vegetation from lakes by acidification may have an indirect effect on a variety of vertebrates: species of fish-eating birds (e.g., the bald eagle, loon, and osprey), fish-eating mammals (e.g., mink and otter), and dabbling ducks which feed on aquatic vegetation. In fact, any animal that depends on aquatic organisms (plant or animal) for a portion of its food may be affected.

Increasing acidity in freshwater habitats results in shifts in species, populations, and communities. Virtually all trophic levels are affected. Summaries of the changes which are likely to occur in aquatic biota with decreasing pH are listed in Tables 7-6 and 7-7.

7.3.2 Terrestrial Ecosystems

Determining the effects of acidic precipitation on terrestrial ecosystems is not an easy task. In aquatic ecosystems, it has been possible to measure changes in pH that occur in acidified waters and then observe the response of organisms living in aquatic ecosystems to the shifts in pH. In the case of terrestrial ecosystems, the situation is more complicated since no components of terrestrial ecosystems appear to be as sensitive to a change in pH as organisms living in poorly buffered aquatic ecosystems. In addition, indirect effects may only be expressed after long periods of time. Nonetheless, the possibility exists that soils and vegetation may be affected, directly or indirectly, by acidic precipitation, albeit in complex ways.

TABLE 7-6. CHANGES IN AQUATIC BIOTA LIKELY TO OCCUR WITH INCREASING ACIDITY

1. Fish populations are reduced or eliminated.

2. Bacterial decomposition is reduced and fungi may dominate saprotrophic communities. Organic debris accumulates rapidly, tying up nutrients and limiting nutrient mineralization and cycling.

3. Species diversity and total numbers of species of aquatic plants and animals are reduced. Acid-tolerant species dominate.

4. Phytoplankton productivity may be reduced due to changes in nutrient cycling and nutrient limitations.

5. Biomass and total productivity of benthic macrophytes and algae may increase due partially to increased lake transparency.

6. Numbers and biomass of herbivorous invertebrates decline. Tolerant invertebrate species, e.g., air-breathing bugs (water-boatmen, back-swimmers, water striders) may become abundant primarily due to reduced fish predation.

7. Changes in community structure occur at all trophic levels.

TABLE 7-7. SUMMARY OF EFFECTS ON AQUATIC ORGANISMS ASSOCIATED WITH A RANGE IN pH

8.0-6.0	· Long-term changes of less than 0.5 pH units in the range 8.0 to 6.0 are likely to alter the biotic composition of freshwaters to some degree. The significance of these slight changes, however, is not great.	Almer et al., 1974; Leivestad et al., 1976; Almer et al., 1978
	· A decrease of 0.5 to 1.0 pH units in the range 8.0 to 6.0 may cause detectable alterations in community composition. Productivity of competing organisms will vary. Some species will be eliminated.	Almer et al., 1974; Leivestad et al., 1976; Conroy et al., 1976; Almer et al., 1978
	· Phytoplankton plentiful and well distributed but numbers of species begin to decrease as pH decreases.	Almer et al., 1974; Kwiatkowski and Roff, 1976; Almer et al., 1978
6.0-5.5	· Decreasing pH from 6.0 to 5.5 will cause a reduction in species numbers and, among remaining species, alterations in ability to withstand stress, and change in species dominance. Reproduction of some salamander species is impaired.	Almer et al., 1974; Leivestad, 1976; Kwaitkowski and Roff, 1976; Almer et al., 1978 Pough and Wilson, 1976
5.5-5.0	· Below pH 5.5, numbers and diversity of species will be reduced. Many species will be eliminated. Crustacean zooplankton, phytoplankton, molluscs, amphipods, most mayfly species, and many stone fly species will begin to drop out. In contrast, several pH-tolerant invertebrates will become abundant, especially the air-breathing forms (e.g., Gyrinidae, Notonectidae, Corixidae), those with tough cuticles which prevent ion losses (i.e., Sialis lutaria), and some forms which live within the sediments (Oligochaeta, Chiromomidae, and Tubificidae). Overall, invertebrate biomass may be reduced.	Almer et al., 1974; Leivestad et al., 1976; Hendrey et al., 1976; Grahn et al., 1974; Grahn, 1976; Kwiatkowski and Roff, 1976; Hagen and Langeland, 1973; Henriksen and Wright, 1977 Hultberg, 1976; Almer et al., 1978
5.0-4.5	· Below pH 5.0, decomposition of organic detritus will be severely impaired. Organic matter accumulates rapidly. Some fungal species increase (Hyphomycetes, basidomycetes). Many fish species are eliminated. (see Table 7-5 for fish species eliminated.)	Leivestad et al., 1976; Schofield, 1976b; Almer et al., 1978 Hall et al., 1980.

TABLE 7-7 (continued)

	· Macrophytes, such as *Lobelia*, are replaced by *Sphagnum* moss.	Leivestad et al., 1976 Hendrey et al., 1976; Grahn et al., 1974; Almer et al., 1978
	· Number of algal species decreases. Acid-tolerant forms remain.	Leivestad et al., 1976; Hendrey et al., 1976; Grahn et al., 1974; Almer et al., 1978
4.5 and below	· Below pH 4.5, all of the above changes will be greatly exacerbated, and all fish will be eliminated. Lower limit for many algal species.	Almer et al., 1974 Leivestad et al., 1976; Schofield, 1976a,b; Wright et al., 1976 Beamish et al., 1975; Menedex, 1976; Trojnar, 1977a,b; Schofield, 1979

Source: Modified from Hendrey (1978).

7.3.2.1 Effects on soils--Acidity is a critical factor in the behavior of natural or agricultural soils. Soil acidity influences the availability of plant nutrients and various microbiological processes which are necessary for the functioning of terrestrial ecosystems; therefore, there is concern that acidic precipitation over time could have an acidifying effect on soils through the addition of hydrogen ions. As water containing hydrogen cations (usually from weak acids) moves through the soil, some of the hydrogen ions replace adsorbed exchangeable cations, such as Ca^{++}, Mg^{++}, K^+, and Na^+ (see Figure 7-26). The removed cations are then carried deep into the soil profile or into the ground water. In native soils hydrogen ions are derived from the following sources (Wiklander, 1979):

1. nutrient uptake by plants--the roots adsorb cation nutrients and desorb H^+;
2. CO_2 produced by plant roots and micro-organisms;
3. oxidation of NH_4^+ and S, FeS_2, and H_2S to HNO_3 and H_2SO_4;
4. very acid litter in coniferous forests, the main acidifying source for the A and B horizons;
5. atmospheric deposition of H_2SO_4 and some HNO_3, NO_x, HCl and NH_4^+ (after nitrification to HNO_3).

In addition to the acidifying factors listed above, the use of ammonium fertilizers on cultivated lands increases the hydrogen cations in the water solution. Ammonium fertilizers are oxidized by bacteria to form nitrate (NO_3^-) and hydrogen ions (H^+) (Donahue et al., 1977). Increased leaching causes soils to become lower in basic Ca^{++}, Mg^{++}, Na^+, and K^+ cations (Donahue et al., 1977). Sensitivity to leaching is according to the following sequence: $Na^+ >> K^+ > Mg^{2+} > Ca^{2+}$ (Wiklander, 1979).

Norton (1977) cited the potential effects of acidic deposition on soils that are listed in Table 7-8. Of those listed, only the increased mobility of cations and their accelerated loss has been observed in field experiments. Overrein (1972) observed an increase in calcium leaching under simulated acid rain conditions, and increased loss by leaching of Ca^{++}, Mg^{++}, and Al^{+3} were observed by Cronan (1980) when he treated New Hampshire soils with simulated acid rain at a pH 4.4.

Wiklander (1979) notes that in humid areas leaching leads to a gradual decrease of plant nutrients in available and mobilizable forms. The rate of nutrient decrease is determined by the buffering capacity of the soil and the amount and composition of precipitation (pH and salt content). Leaching sooner or later leads to soil acidification unless the buffering capacity of the soil is great and/or the salt concentration of precipitation is high. Soil acidification influences the amount of exchangeable nutrients and is also likely to affect various biological processes in the soil.

Acidic precipitation increases the amounts of SO_4^{2-} and NO_3^- entering the soils. Nitrate is easily leached from soil; however, because it is usually deficient in the soil for both

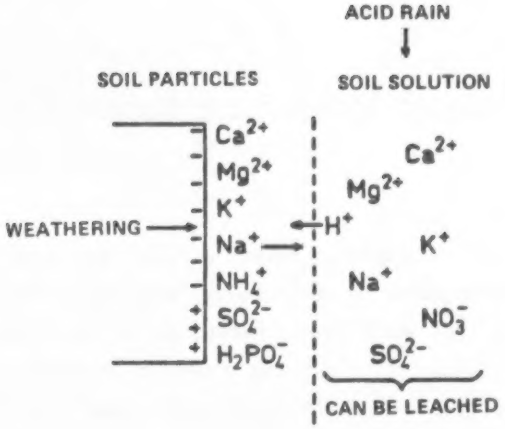

ACID RAIN
SOIL PARTICLES
SOIL SOLUTION
Ca^{2+}
Mg^{2+}
K^+
WEATHERING
Na^+
NH_4^+
SO_4^{2-}
$H_2PO_4^-$
H^+
Ca^{2+}
Mg^{2+}
K^+
Na^+
NO_3^-
SO_4^{2-}
CAN BE LEACHED

Figure 7-26. Showing the exchangeable ions of a soil with pH 7, the soil solution composition, and the replacement of Na^+ by H^+ from acid rain.

Source: Wiklander (1979).

TABLE 7-8. POTENTIAL EFFECTS OF ACID PRECIPITATION ON SOILS

Effect	Comment
Increased mobility of most elements	Mobility changes are essentially in the order: monovalent, divalent, trivalent cations.
Increased loss of existing clay minerals	Under certain circumstances may be compensated for by production of clay minerals which do not have essential (stoichiometric) alkalies or alkali earths.
A change in cation exchange capacity	Depending on conditions, this may be an increase or a decrease.
A general proportionate increase in the removal of all cations from the soil	In initially impoverished or unbuffered soil, the removal may be significant on a time scale of 10 to 100 years.
An increased flux in nutrients through the ecosystem below the root zone	

Source: Norton (1977).

plants and soil microorganisms, it is rapidly taken up and retained within the soil-plant system (Gjessing et al., 1976; Abrahamsen et al., 1976; Abrahamsen and Dollard, 1979). The fate of sulfate is determined by its mobility. Retention of sulfate in soils appears to depend on the amount of hydrous oxides of iron and aluminum present. The amounts of these compounds present varies with the soil type. Insignificant amounts of the hydrated oxides of iron (Fe) and aluminum (Al) are found in organic soils; therefore, sulfate retention is low (Abrahamsen and Dollard, 1979). The presence of hydrated oxides of iron and aluminum, however, is only one of the factors associated with the capability of a soil to retain sulfur. The capacity of soils to adsorb and retain anions increases as the pH decreases and with the salt concentration. Polyvalent anions of soluble salts added experimentally to soils increase adsorption and decrease leaching of salt cations. The effectiveness of the anions studied in preventing leaching increased in the following order: $Cl^- \sim NO_3^- < SO_4^{2} < H_2PO_4^-$ (Wiklander, 1980). Additions of sulfuric acid to a soil will have no effect on cation leaching unless the sulfate anion is mobile, as cations cannot leach without associated anions (Johnson et al. 1980; Johnson, 1980; Johnson and Cole, 1980).

Leaching of soil nutrients is efficiently inhibited by vegetation growing on it. Plant roots take up the nutrients frequently in larger amounts than required by the plants. Large amounts of these nutrients will later be deposited on the soil surface as litter or as leachate from the vegetation canopy (Abrahamsen and Dollard, 1979).

In lysimeter experiments in Norway, plots with vegetation cover were used. One plot had a dense layer of the grass, Deschampsia flexuosa (L.) Trin. and the other a less dense cover. The soil retained approximately 50 percent of the SO_4^{2-} added to it. The greatest amount was retained in the lysimeters covered with grass; the relative retention increased with increasing additions of sulfate (Abrahamsen and Dollard, 1979). Leaching of cations from the soil was reduced by the retention of the SO_4^{2-}; however, leaching of Ca^{2+} and Mg^{2+} increased significantly as the acidity of the simulated rain increased. In the most acid treatment leaching of Al was highly significant. The behavior of K^+, NO_3^-, and NH_4^+ was different in the two lysimeter series. These ions were retained in the grass-covered lysimeters whereas there was a net leaching of K^+ and NO_3^- in the other series. Statistically significant effects were obtained only when the pH of the simulated rain was 3.0 or lower (Abrahamsen and Dollard, 1979).

The Scandinavian lysimeter experiments appear to demonstrate that the relative rate of adsorption of sulfate increases as the amounts applied are increased. In the control lysimeters the output/input ratio was approximately one. These results are in agreement with results of watershed studies which frequently appear to demonstrate that, on an annual basis, sulfate outflow is equal to or greater than the amounts being added (Gjessing et al., 1976; Abrahamsen and Dollard, 1979). Increased outflow may be attributed to dry deposition and the weathering of sulfur-bearing rocks. The increased deposition of sulfate via acidic precipitation appears to have increased the leaching of sulfate from the soil. Together with the retention of hydrogen ions in the soil this results in an increased leaching of the nutrient cations K^+, Ca^{2+}, Mg^{2+}, and Mn (Abrahamsen and Dollard, 1979). Shriner and Henderson (1978), however, in their study of sulfur distribution and cycling in the Walker Branch Watershed in eastern Tennessee noted the additions of sulfate sulfur by precipitation were greater than the amount lost in stream flow. Analysis of the biomass and soil concentrations of sulfur indicated that sulfur was being retained in the mineral soil horizon. It is suggested that leaching from organic soil horizons may be the mechanism by which sulfur is transferred to the mineral horizon. Indirect evidence suggests that vegetation scavenging of atmospheric sulfate plays an important role by adding to the amounts of sulfur entering the forest system over wet and dry deposition.

Studies of the nutrient cycling of sulfur in a number of forest ecosystems indicate that some ecosystems accumulate (Johnson et al., 1980; Heinrichs and Mayer, 1977; Shriner and Henderson, 1978) while other ecosystems maintain a balance between the additions and losses of sulfur or show a net loss (Cole & Johnson, 1977). Sulfur accumulation appears to be associated with sulfate adsorption in subsoil horizons. Sulfate adsorption is strongly dependent on pH.

Little adsorption occurs above pH 6-7 (Harward and Reisenaur, 1966). The amount of sulfate in a soil is a function of a soil's adsorption properties and the amount of sulfate that has been added to the soil, integrated over time. Soil properties may favor the adsorption of sulfate; however, the net annual accumulation of sulfate at any specific time will be influenced by the degree of soil saturation (Johnson et al., 1980).

Lowered soil pH also influences the availability and toxicity of metals to plants. In general, potentially toxic metals become more available as pH decreases. Ulrich (1975) reported that aluminum released by acidified soils could be phytotoxic if acid rain continued for a long period. The degree of ion leaching increased with decreases in pH, but the amount of cations leached was far less than the amount of acid added (Malmer, 1976). Baker et al. (1977) found that sulfur dioxide in precipitation increased the extractable acidity and aluminum, and decreased the exchangeable bases, especially calcium and magnesium. Although dilute sulfuric acid in sandy podsolic soils caused a significantly decreased pH of the leached material, the amount of acid applied (not more than twice the yearly airborne supply over southern Scandinavia) did not acidify soil as much as did nitrate fertilizer (Tamm et al., 1977). Highly acidic rainfall, frequently with a pH less than 3.0, in combination with heavy metal particulate fallout from smelters, has caused soils to become toxic to seedling survival and establishment according to observations by Hutchinson and Whitby (1976). Very low soil pH's are associated with mobility of toxic aluminum compounds in the soils. High acidity, high sulfur, and heavy metals in the rainfall have caused fundamental changes in the structure of soil organic matter. The sulfate and heavy metals were borne by air from the smelters in the Sudbury area of Ontario and brought to earth by dry and wet deposition. Among the metals deposited in rainfall and dustfall were nickel, copper, cobalt, iron, zinc, and lead. Most of these metals are retained in the upper layers of soil, except in very acid or sandy soils.

The accumulation of metals in soils is mainly an exchange phenomenon. Organic components of litter, humus, and soil may bind heavy metals as stable complexes (Tyler, 1972). The heavy metals when bound may interfere with litter decay and nutrient cycling, and in this manner interfere with ecosystem functioning (Tyler, 1972). Acidic precipitation, by altering the equilibria of the metal complexes through mobilization, may decrease the residence time of the heavy metals in soil and litter (Tyler, 1972, 1977).

Biological processes in the soil necessary for plant growth can be affected by soil acidification. Nitrogen fixation, decomposition of organic material, and mineralization, especially of nitrogen, phosphorus and sulfur, could be affected (Abrahamsen and Dollard, 1979; Tamm et al., 1977; Malmer, 1976; Alexander, 1980). Nearly all of the nitrogen, most of the phosphorus and sulfur, as well as other nutrient elements in the soil are bound in organic combination. In this form, the elements are largely or entirely unavailable for utilization by higher plants (Alexander, 1980). It is principally through the activity of heterotrophic microorganisms that nitrogen, phosphorus, and sulfur are made available to the autotrophic higher plants. Thus, the microbial processes that lead to the conversion of the organic forms of these elements to the inorganic state are crucial for maintaining plant life in natural or agricultural ecosystems. The key role of these degradative processes is illustrated by the fact that nitrogen is limiting for food production in much of the world and governs primary productivity in many terrestrial habitats (Alexander, 1980).

Many, and probably most, microbial transformations in soil may be brought about by several species. Therefore, the reduction or elimination of one population is not necessarily detrimental since a second population, not affected by the stress, may fill the partially or totally vacated niche. On the other hand, there are a few processes that are carried out, so far as it is now known, by only a single species, and elimination of that species could have serious consequences. Examples of this are nitrification in which ammonium is converted to nitrate, and nodulation of leguminous plants, for which the bacteria are reasonably specific according to the leguminous host (Alexander, 1980).

Nitrification is one of the best indicators of pH stress because the responsible organisms, presumably largely autotrophic bacteria, are sensitive both in culture and in nature to increasing acidity (Dancer et al., 1973). Although nitrification will sometimes occur at pH values below 5.0, characteristically the rate decreases with increasing acidity and often is undetectable much below pH 4.5. Limited data suggest that the process of sulfate reduction to sulfide in soil is markedly inhibited below a pH of 6.0. (Connell and Patrick, 1968) and studies of the presumably responsible organisms in culture attest to the inhibition linked with the acid conditions (Alexander, 1980).

It is difficult to make generalizations concerning the effects of soil acidification on microorganisms. Many microbial processes that are important for plant growth are clearly suppressed as the pH declines; however, the inhibition noted in one soil at a given pH may not be noted at the same pH in another soil (Alexander, 1980). The capacity of some microorganisms to become acclimated to changes in pH suggests the need to study this phenomenon using environments that have been maintained at different pH values for some time. Typically the studies have been done with soils maintained only for short periods at the greater acidity (Alexander, 1980). The consequences of increased acidity in the subterranean ecosystem are totally unclear, however; the pH of soil influences not only the microbial community at large, but also those specialized populations that colonize the root surfaces (Alexander, 1980).

The addition of nitrate and other forms of nitrogen from the atmosphere to ecosystems through the activity of microorganisms is an integral function of the terrestrial nitrogen cycle. The contribution of inorganic nitrogen in wet precipitation (rain plus snow) is usually equivalent to only a few percent of the total nitrogen assimilated annually by plants in terrestrial ecosystems; however, total nitrogen contributions, including organic nitrogen, in bulk precipitation (rainfall plus dry fallout) can be significant, especially in unfertilized natural systems.

Atmospheric contributions of nitrate can range from less than 0.1 kg N/ha/yr in the Northwest (Fredricksen, 1972) to 4.9 kg N/ha/yr in the Eastern United States (Likens et al., 1970; Henderson and Harris, 1975). Inorganic nitrogen (ammonia-N plus nitrate-N) additions in wet precipitation ranged from less than 0.5 kg/ha/yr to more than 3.5 kg/ha/yr in Junge's (1958) study of rainfall over the United States. On the other hand, total nitrogen loads in bulk precipitation range from less than 5 kg/ha/yr in desert regions of the West to more than 30 kg/ha/yr near barnyards in the Midwest. Total contributions of nitrogen from the atmosphere commonly range from about 10 to 20 kg N/ha/yr for most of the United States (National Research Council, 1978).

In comparison, rates of annual uptake by plants in ecosystems selected from several bioclimatic zones; (deciduous forest, tundra, desert, western coniferous forest, grassland and tropical forest) range from 11 to 125 kg N/ha/yr. (National Research Council, 1978). Since the lowest additions are generally associated with desert areas where rates of uptake by plants are low, and the highest additions usually occur in moist areas where plant uptake is high, the contributions of ammonia and nitrate from rainfall to terrestrial ecosystems are equivalent to about 1 to 10 percent of annual plant uptake. In eastern deciduous and western coniferous forest ecosystems, contributions from bulk precipitation, on the other hand, represent from about 8 to 25 percent of the annual plant requirements. Although these comparisons suggest that plant growth in terrestrial ecosystems depends to a significant extent on atmospheric deposition, it is not yet possible to estimate the importance of these contributions by comparing them with the biological fixation and mineralization of nitrogen in the soil. In nutrient-impoverished ecosystems, such as badly eroded abandoned croplands or soils subjected to prolonged leaching by acidic precipitation, nitrogen additions from atmospheric depositions are certainly important to biological productivity. In largely unperturbed forests, recycled nitrogen from the soil organic pool is the chief source of nitrogen for plants, but nitrogen to support increased production must come either from biological fixation or from atmospheric contributions. It seems possible, therefore, that man-generated contributions could play a significant ecological role in a relatively large portion of the forested areas near industrialized regions (Galloway, 1978).

Sulfur, like nitrogen, is essential for optimal plant growth. Plants usually obtain sulfur from the soil in the form of sulfate. The amount of mineral sulfur in soils is usually low and its release from organic matter during microbial decomposition is a major source for plants (Donahue et al., 1977). Another major source is the wet and dry deposition of atmospheric sulfur (Donahue et al., 1977; Brady, 1974; Jones, 1975).

In agricultural soils crop residues, manure, irrigation water, fertilizers, and soil amendments are important sources of sulfur. The amounts of sulfur entering the soil system from atmospheric sources is dependent on proximity to industrial areas, the sea coast, and marshlands. The prevailing winds and the amount of precipitation in a given region are also important (Halstead and Rennie, 1977). Near fossil-fueled power plants and industrial sources, the amount of sulfur in precipitation may be as much as 150 pounds per acre (168 kg/ha) or more (Jones, 1975). By contrast, in rural areas, based on the equal distribution of sulfur oxide emissions over the coterminous states, the amount of sulfur in precipitation is generally well below the average 15 pounds per acre (17 kg/ha). Approximately 5 to 7 pounds per acre (7 to 8 kg/ha) per year were reported for Oregon in 1966 (Jones, 1975). Shinn and Lynn (1979) have estimated that in the Northeastern United States, the area where precipitation is most acidic, approximately 5 x 10^6 tons of sulfate per year is removed by rain. Hoeft et al. (1972) estimated the overall average sulfur as sulfate deposition at 26 pounds of sulfur per acre per year (30 kg S/ha/year). Estimates for rural areas were 14 pounds of sulfur per acre per year (16 kg/ha/yr). Approximately 40 to 50 percent of the sulfur additions occurred from November to February. Tabatabai and Laflen (1976) found that SO_4-S deposition in Iowa was greatest in fall and winter when precipitation was low.

Experimental data have shown that even though plants are supplied with adequate soil sulfate they can absorb 25 to 35 percent of their sulfur from the atmosphere (Brady, 1974). Particularly if the soil sulfur is low and atmospheric sulfur is high, most of the sulfur required by the plant can come from the atmosphere (Brady, 1974). Atmospheric sulfur would be of benefit chiefly to plants growing on lands with a low sulfur content (Brezonik, 1976).

Tree species vary in their ability to utilize sulfur. Nitrogen and sulfur are biochemically associated in plant proteins, therefore, a close relationship exists between the two in plants. Apparently, nitrogen is only taken up at the rate at which sulfur is available. Protein formation, therefore, is limited by the amount of sulfur available (Turner and Lambert, 1980). Conifers accumulate as sulfate any sulfur beyond the amount required to balance the available nitrogen. Protein formation proceeds at the rate at which nitrogen becomes available. Trees are not injured when sulfur is applied as sulfate rather than SO_2 (Turner and Lambert, 1980).

When discussing the effects of acidic precipitation, or the effects of sulfates or nitrates on soils, a distinction should be made between managed and unmanaged soils. There appears to be general agreement that managed agricultural soils are less susceptible to the influences of acidic precipitation than are unmanaged forest or rangeland soils. On managed soils more than adequate amounts of lime are used to counteract the acidifying effects of fertilizers in agricultural soils. Ammonium fertilizers, usually as ammonium sulfate $[(NH_4)_2SO_4]$ or ammonium nitrate, (NH_4NO_3) are oxidized by bacteria to form sulfate (SO_4^{2-}) and/or nitrate (NO_3^-) and hydrogen ions (H^+) (Donahue et al. 1977; Brady, 1974). The release of hydrogen ions into the soil causes the soil to become acidified. Hydrogen ions are also released into the soil when plants take up mineral nutrients. Hence, substances (notably various complexes of ammonium and sulfate ions), although of neutral pH, or nearly so, are acidifying in their effects when they are taken up by plants or animals. Thus, the concept of "acidifying precipitation" must be added to the concept of "acid precipitation."

The acidifying effects of fertilization or acidic precipitation is countered in managed soils through the use of lime. Liming tends to raise the pH and thereby eliminate most major problems associated with acidic soils (Donahue et al., 1977; Likens et al., 1977). Costs of liming all natural soils sensitive to acidification would be prohibitive as well as extremely difficult to carry out.

Precipitation adds many chemicals to terrestrial, aquatic, and agricultural ecosystems. In addition to sulfur and nitrogen, phosphorus and potassium are biologically most important because they often are in limited supply in the soil (Likens et al., 1977). Other chemicals of varying biological importance and varying concentration found in precipitation over North America are the following: chlorine, sodium, calcium, magnesium, iron, nickel, copper, zinc, cadmium, lead, manganese (Beamish, 1976; Hutchinson and Whitby, 1976; Brezonik, 1976), mercury (Brezonik, 1976), and cobalt (Hutchinson and Whitby, 1976). Rain over Britain and the Netherlands, according to Gorham (1976), contained the following elements in addition to those reported for North American precipitation: aluminum, arsenic, beryllium, cerium, chromium, cesium, antimony, scandium, selenium, thorium, and vanadium. Again, it is obvious that many of these elements will be found in precipitation in highly industrialized areas and will not be of biological importance until they enter an ecosystem where they may come into contact with some form of life, as in the case of heavy metals in the waters and soils near Sudbury, Ontario. Of the chemical elements found in precipitation, magnesium, iron, copper, zinc, and manganese are essential in small amounts for the growth of plants; however, at high concentrations these elements, as well as the other heavy metals, can be toxic to plants and animals. Furthermore, the acidity of precipitation can affect the solubility, mobility, and toxicity of these elements to the foliage or roots of plants and to animals or microorganisms that may ingest or decompose these plants.

Wiklander (1979) has pointed out that based on the ion exchange theory, ion exchange experiments, and the leaching of soil samples, the following conclusions can be drawn about the acidifying effect on soils through the atmospheric deposition of mineral acids:

1. At a soil pH > 6.0, acids are fully neutralized by decomposition of $CaCO_3$ and other unstable minerals and by cation exchange.
2. At soil pH < 5.5, the efficiency of the proton to decompose minerals and to replace exchangeable Ca^{2+}, Mg^{2+}, K^+, and Na^+ decreases with the soil pH. Consequently, the acidifying effect of mineral acids on soils decreases, but the effect on the runoff water increases in the very acid soils.
3. Salts of Ca^{2+}, Mg^{2+}, K^+, and NH_4^+ in the precipitation counteract the absorption of protons and, in that way, the decrease of the base saturation. A proportion of the acids percolate through the soil and acidify the runoff.

The sensitivity of various soils to acidic precipitation depends on the soil buffer capacity and on the soil pH. Noncalcareous sandy soils with pH > 5 are the most sensitive to acidification; however, acidic soils would be most likely to release aluminum.

Very acid soils are less sensitive to further acidification because they are already adjusted by soil formation to acidity and are therefore more stable. In these soils easily weatherable minerals have disappeared, base saturation is low, and the pH of the soil may be less than that of precipitation. The low nutrient level is a crucial factor which limits productivity in these soils. Even a slight decrease in nutrient status by leaching may have a detrimental effect on plant yield (Wiklander, 1979). Fertilization appears to be the only preventive measure.

In properly managed cultivated soils, acidic precipitation should cause only a slight increase in the lime requirement, with a cost compensated for by the supply of sulfur, nitrogen, magnesium, potassium, and calcium made available to plants (Wiklander, 1979).

7.3.2.2 Effects on vegetation--The atmosphere, as well as the soil, is a source of nutrients for plants. Chemical elements reach the plant surface via wet and dry deposition. Nitrates and sulfates are not the only components of precipitation falling onto the plant surface. Other chemical elements (cadmium, lead, zinc, and manganese), at least partially soluble in water, are deposited on the surface of vegetation and may be assimilated by it, usually through the leaves. (See Chapter 8 for discussion of particulate matter.) An average raindrop deposited on trees in a typical forest washes over three tiers of foliage before it reaches the soil. The effects of acidic precipitation may be beneficial or deleterious depending on its chemical composition, the species of plant on which it is deposited, and the physiological condition and maturity of the plant (Galloway and Cowling, 1978). Substances accumulated on the leaf surfaces strongly influence the chemical composition of precipitation not only at the leaf surface, but also when it reaches the forest floor. The chemistry of precipitation reaching the forest floor is considerably different from that collected above the forest canopy or a ground level where the canopy has no influence (Lindberg et al. 1979). Except for the hydrogen ion (H^+) the mean concentrations of all elements (lead, manganese, zinc and cadmium) studied in the Walker Branch Watershed in Tennessee were found by Lindberg et al. (1979) to be present in greater amounts in the throughfall than in incident rain. Their study indicated that the presence of trace elements was more variable than that of the sulfate and hydrogen ions and that throughfall appeared to be a more dilute solution of sulfuric acid than rain with a pH $\sim$ 4.5 not influenced by the forest canopy. The solution was found to contain a relatively higher concentration of alkaline earth salts of sulfate and nitrate as well as a somewhat higher concentration of trace elements (Lindberg et al. 1979).

Lee and Weber (1980) studied the effects of sulfuric acid rain on two model hardwood forests. The experiment, conducted under controlled field conditions, consisted of the application of simulated sulfuric acid rain (pH values of 3.0, 3.5, and 4.0), and a control rain of pH 5.6 to the two model forest ecosystems for a duration of 3 and 1/2 years. Rainfall applications approximated the annual amounts of areas in which sugar maple and red alder communities normally occur.

In evaluating the results of the study, the authors conclude that a well developed forest canopy and litter layer can increase the pH and concentration of bases (i.e., calcium and magnesium) in rainwater. Such conditions would tend to decrease the acidification rate of forest soils by acid rain. However, as bases are continually leached from the soil column, these cations could eventually be lost from the ecosystem and unavailable to influence the acidification reactions. Changes in the ionic and pH balance of forest systems may impact the productivity of forests through acidity-induced changes in the nutrient cycling process, decomposition, reproduction, tree growth, and structure of forest systems (Alexander, 1980).

The additions of hydrogen, sulfate and nitrate ions to soil and plant systems have both positive and negative effects. It has generally been assumed that the free hydrogen ion concentration in acidic precipitation is the component that is most likely to cause direct, harmful effects on vegetation (Jacobson, 1980a). Experimental studies support this assumption; however, to date, there are no confirmed reports of exposure to ambient acidic precipitation causing foliar symptoms on field grown vegetation in the continental United States (Jacobson, 1980a) or Canada (Linzon personal communication 1980).

7.3.2.2.1 Direct effects on vegetation. Hydrogen ion concentrations equivalent to that measured in more acidic rain events ($\leq$ pH 3.0) have been observed experimentally through the use of simulated acid rain to cause tissue injury in the form of necrotic lesions to a wide variety of plant species under greenhouse and laboratory conditions. This visible injury has been reported as occurring between pH 3.0 and 3.6 (Shriner, 1980). The various types of direct effects which have been reported are shown in Table 7-9. Such effects must be interpreted with caution because the growth and morphology of leaves on plants grown in greenhouses frequently are atypical of field conditions (Shriner, 1980). (See Chapter 8 for discussion of the vegetational effects of SO_2).

Small necrotic lesions, the most common form of direct injury, appear to be the result of the collection and retention of water on plant surfaces and the subsequent evaporation of these water droplets which concentrates the solution's constituents causes a lesion to occur. The depression formed by the lesion further enhances the collection of water. A large percentage of the leaf area may exhibit lesions after repeated exposures to simulated acid rain at pH concentrations of 3.1, 2.7, 2.5 and 2.3 (Evans et al. 1977a, 1977b). In leaves injured by simulated acidic rain, collapse and distortion of epidermal cells on the upper surface is frequently followed by injury to the palisade cells and ultimately both leaf surfaces are affected (Evans et al., 1977b). Evans et al. (1978), using six clones of Populus spp. hybrids, found that leaves that had just reached full expansion were more sensitive to simulated acid rain at pH 3.4, 3.1, 2.9, and 2.7 than those which were unexpanded or fully expanded. On two of the clones, gall formation due to abnormal cell proliferation and enlargement occurred. Other effects attributed to simulated acid rain include the modification of the leaf surface, e.g. epicuticular waxes, and alteration of physiological processes such as carbon fixation and allocation.

TABLE 7-9. TYPES OF DIRECT, VISIBLE INJURY REPORTED IN RESPONSE TO SIMULATED ACIDIC WET DESPOSITION

Injury Type	Species	pH Range	Reference	Remarks
Pitting, curl shortening, death	Yellow birch	2.3-4.7	Wood and Bormann, 1974	
1-mm necrotic lesions, premature abscission	Kidney bean, soybean, loblolly pine, E. white pine, willow oak	3.2	Shriner et al., 1974	
Cuticular erosion	Willow oak	3.2	Shriner, 1978a, Lang et al., 1978	
Chlorosis	Sunflower, bean	2.3-5.7	Evans et al., 1977b	
(A) small, shallow circular depressions: slight chlorosis	Sunflower, bean	2.7	Evans et al., 1977b	More frequent near veins. (A) - (D) represent sequential stages of lesion development, through time, up to 72 hrs (one 6-min rain event daily for 3 days)
(B) larger lesions, chlorosis always present palisade collapse	Sunflower, bean	2.7	Evans et al., 1977b	
(C) 1-mm necrotic lesions general distortion	Sunflower, bean	2.7	Evans et al., 1977b	
(D) 2-mm bifacial necrosis sue to coalescence of smaller lesions, total tissue collapse.	Sunflower, bean	2.7	Evans et al., 1977b	
Wrinkled leaves, excessive adventitious budding, premature abscission	Bean	1.5-3.0	Ferenbaugh, 1976	

TABLE 7-9 (continued)

Injury Type	Species	pH Range	Reference	Remarks
Incipient bronzed spot	Bean	2.0-3.0	Hindawi et al., 1980	After first few hours
Bifacial necrotic pitting	Bean	2.0-3.0	Hindawi et al., 1980	After 24 h (reported pooling of drops = more injury)
Necrotic lesions, premature abscission	E. white pine, scotch pine, spinach, sunflower, bean	2.6-3.4	Jacobson and van Leuken, 1977	Injury associated with droplet location within 24-48 h.
Marginal and tip necrosis	Bean, poplar, soybean, ash birch, corn, wheat	Submicron H_2SO_4 aerosol	Lang et al., 1978	
Galls, hypertrophy, hyperplasia	Hybrid poplar	2.7-3.4	Evans et al., 1978	
Dead leaf cells	Soybean	3.1	Irving, 1979	

Source: Shriner, 1980

Lee et al. (1980) studied the effects of simulated acidic precipitation on crops. Depending on the crop studied, they reported beneficial, detrimental or no effects on yield when crops were exposed to sulfuric acid rain at pH values of 3.0, 3.5, and 4.0 and were compared to crops exposed to a control rain of pH 5.6. The yield of tomatoes, green peppers, strawberries, alfalfa, orchard grass, and timothy were stimulated. Yields of radishes, carrots, mustard greens, and broccoli were inhibited. Potatoes were ambiguously affected except at pH 3.0 where their yield, as well as that of beets, was inhibited. Visible injury of tomatoes might have decreased their market value. In sweet corn, stem and leaf production was stimulated, but no statistically significant effects on yield were observed for 15 other crops. Results suggest that the possibility of acid rain affecting yield depends on the portion of the plant being commercially utilized as well as the species. Plants were regularly examined for foliar injury associated with acid rain. Of the 35 cultivars examined, the foliage of 31 was injured at pH 3.0; 28 at pH 3.5; and 5 at pH 4.0. Foliar injury was not generally related to effects on yield. However, foliar injury of swiss chard, mustard greens, and spinach was severe enough to adversely affect marketability. These results are from a single growing season and therefore considered to be preliminary.

Studies indicate that wet deposition of acidic or acidifying substances may result in a range of direct or indirect effects on vegetation. Environmental conditions before, during and after a precipitation event affect the responses of vegetation. Nutrient status of the soil, plant nutrient requirements, plant sensitivity, growth stage and the total loading or deposition of critical ions (e.g. H^+, NO_3^- and SO_4^- all play a role in determining vegetational response to acidic precipitation).

Wettability of leaves appears to be an important factor in the response of plants to acid deposition. This has been demonstrated in the work of Evans and Curry (1977), Jacobson and van Leuken (1977), and Shriner (1978a), who variously report a threshold of between pH 3.1 and 3.5 for development of foliar lesions on beans. The cultivars of Phaseolus vulgaris L. used in the above studies are all relatively non-waxy and therefore fairly easily wettable. By comparison, studies with the very waxy leaves of citrus (Heagle et al., 1978) reported a threshold for visible symptoms to be near pH 2.0. Waxy leaves apparently minimize the contact time for the acid solutions, thus accounting for the <400X increase in H^+ ion concentration required to induce visible injury. Table 7-10 summarizes the thresholds, species sensitivity, concentration, and time for visible injury associated with experimental studies of wet deposition of acidic substances.

Leaching of chemical elements from exposed plant surfaces is an important effect that rain, fog, mist, and dew have on vegetation. Substances leached include a great diversity of materials. All of the essential minerals, amino acids, carbohydrate growth regulators, free sugars, pectic substances, organic acids, vitamins, alkaloids, and allelopathic substances are among the materials which have been detected in plant leachates (Tukey, 1970). Many factors

TABLE 7-10. THRESHOLDS FOR VISIBLE INJURY AND GROWTH EFFECTS ASSOCIATED WITH EXPERIMENTAL STUDIES OF WET DEPOSITION OF ACIDIC SUBSTANCES (AFTER JACOBSON, 1980a,b)

Effect	Species	Threshold[1]	Reference	Remarks
Foliar lesions, decrease in growth	Yellow birch	pH 3.1	Wood and Bormann (1974)	greenhouse
Foliar aberrations, decrease in growth	Bean	pH 2.5	Ferenbaugh (1976)	greenhouse
Foliar lesions	Bean, sunflower	pH 3.1	Evans et al. (1977a)	greenhouse
Foliar lesions	Bean	pH 3.2	Shriner (1978a)	greenhouse
Foliar lesions	Hybrid poplar	pH 3.4	Evans et al. (1978)	greenhouse
Foliar lesions	Sunflower	pH 3.4	Jacobson and van Leuken (1977)	greenhouse
Foliar symptons, no reduced growth	Soybean	pH 3.0	Jacobson (1980b)	greenhouse
Increased growth, increased/decreased nutrient content	Lettuce	pH 3.0, 3.2	Jacobson (1980b)	greenhouse (varied with $SO_4^=$ & NO_3^-)
Reduced growth	Pinto bean	pH 3.1	Jacobson (1980b)	greenhouse
Reduced yield	Pinto bean	pH 2.7	1/m	1/m
Reduced growth	Soybean	pH 3.1	1/m	1/m
Reduced yield	Soybean	pH 2.5	1/m	1/m

TABLE 7-10 (continued)

Effect	Species	Threshold[1]	Reference	Remarks
Increased yield	Soybean	pH 3.1		
Foliar symptoms	Tomato	pH 3.0	Jacobson (1980b)	greenhouse
Reduced growth	Tomato	pH 3.0		
Reduced yield	Tomato	pH 3.0		
Reduced quality	Tomato	pH 3.0		
No foliar symptoms, or effects on growth	Soybean	pH 3.1	Irving (1979)	field
No foliar symptoms, but	Soybean	pH 2.8	Jacobson (1980b)	field, low ozone
a) decreased growth, yield	Soybean	pH 2.8		field, high ozone
b) increased yield	Soybean	pH 2.8		field, low ozone
No effect on growth, yield	Tomato	pH 3.0	Jacobson (1980b)	field
Reduced quality	Tomato	pH 3.0		field

[1] Highest pH to elicit a negative growth response, or lowest pH to elicit a positive growth response

Shriner, 1980.

influence the quantity and quality of the substances leached from foliage. They include factors associated directly with the plant as well as those associated with the environment. Not only are there differences among species with respect to leaching, but individual differences also exist among individual leaves of the same crop and even the same plant, depending on the physiological age of the leaf. Young, actively growing tissues are relatively immune to leaching of mineral nutrients and carbohydrates, while mature tissue which is approaching senescence is very susceptible. The stage of plant development, temperature, and rainwater falling on foliage and running down plant stems or tree bark influences leaching. Rainwater, which naturally has a pH of about 5.6, washing over vegetation may become enriched with substances leached from the tissues (Nihlgård, 1970).

Leaching of organic and inorganic materials from vegetation to the soil is part of the normal functioning of terrestrial ecosystems. The nutrient flow from one component of the ecosystem to another is an important phase of nutrient cycling (Comerford and White, 1977; Eaton et al., 1973). Plant leachates have an effect upon soil texture, aeration, permeability, and exchange capacity. Leachates, by influencing the number and behavior of soil microorganisms, affect soil-forming processes, soil fertility, and susceptibility or immunity of plants to soil pests and plant-chemical interactions (Tukey, 1970).

It has been demonstrated under experimental conditions that precipitation of increased acidity can increase the leaching of various cations and organic carbon from the tree canopy (Abrahamsen et al., 1976; Wood and Bormann, 1975). Foliar losses of potassium, magnesium, and calcium from bean plants and maple seedlings were found to increase as the acidity of an artificial mist was increased. Below a pH of 3.0 tissue damage occurred; however, significant increases in leaching were measured at pH 3.3 and 4.0 with no observable tissue damage (Wood and Bormann, 1975). Hindawi et al. (1980) also noted that, as the acidity of sulfuric acid mist increased, so did the foliar leaching of nitrogen, calcium, phosphorous, and magnesium. Potassium concentrations were not affected, while the concentration of sulfur increased. Abrahamsen and Dollard (1979), in experiments using Norway spruce (_Picea_ _abies_ L. Karst), observed that despite increased leaching under the most acid treatment, there was no evidence of change in the foliar cation content. Wood and Bormann (1977), using Eastern white pine (_Pinus_ _strobus_ L.), also noted no significant changes in calcium, magnesium or potassium content of needles. Tukey (1970) states that increased leaching of nutrients from foliage can accelerate nutrient uptake by plants. No injury will occur to the plants as long as roots can absorb nutrients to replace those being leached; however, injury could occur if nutrients are in short supply. To date, the effects, if any, of the increased leaching of substances from vegetation by acidic precipitation remain unclear.

Some experimental evidence suggests that acidic solutions affect the chlorophyll content of leaves and the rate of photosynthesis. Sheridan and Rosenstreter (1973) reported marked reduction of photosynthesis in a moss exposed to increasing H^+ ion concentrations. Sheridan and Rosenstreter (1973), Ferenbaugh (1976), and Hindawi et al. (1980) reported reduced chlorophyll content as a result of tissue exposure to acid solutions. In the case of Ferenbaugh (1976), however, the significant reductions in chlorophyll in the leaves of Phaseolus vulgaris at pH 2.0 were associated with large areas of necrosis. A significant aspect of this study was the loss of capacity by the plant to produce carbohydrates. The rate of respiration in these plants showed only a slight, but significant increase, while the rate of photosynthesis at pH 2.0 increased nearly fourfold as determined by oxygen evolution. Ferenbaugh concluded that due to a reduction in biomass accumulation and sugar and starch concentrations, photophosphorylation in the treated plants was in some way being uncoupled by the acidic solutions.

Irving (1979) reported a higher chlorophyll content and an increased rate of photosynthesis in field-grown soybeans exposed to simulated rain at pH 3.1. She attributed the increases to improved nutrition due to the sulfur and nitrogen components of the simulated acid rain overcoming any negative effects.

Vegetation is commonly exposed to gaseous phytotoxicants such as ozone and sulfur dioxide at the same time as acidic precipitation. Little information is available upon which to evaluate the potential for determining the effects of the interaction of wet-and dry-deposited pollutants on vegetation. Preliminary studies by Shriner (1978b), Irving (1979), and Jacobson et al. (1980) suggest that interactions may occur. Irving (1979) found that simulated acid precipitation at pH of 3.1 tended to limit the decrease in photosynthesis observed when field -grown soybeans were exposed 17 times during the growing season to 500 $\mu g/m^3$ (0.19 ppm) of SO_2. Shriner (1978b), however, reported no significant interaction between multiple exposure to simulated rain at pH 4.0 and four SO_2 exposures (17860 $\mu g/m^3$, 3 ppm peak for 1 hr.) upon the growth of bush beans. Shriner (1978b) also exposed plants to 290 $\mu g/m^3$ (0.15 ppm) ozone (4 3-hour exposures) in between 4 weekly exposures to rainfall of pH 4.0, and observed a significant growth reduction at the time of harvest. Jacobson et al. (1980b), using open-top exposure chambers with field-grown soybeans, compared growth and yield between three pH levels of simulated rain (pH 2.8, 3.4, and 4.0) and two levels of ozone (<60 and ≤ 240 $\mu g/m^3$, <0.03 and ≤ 0.12 ppm). Results demonstrated that ozone not only depressed both growth and yield of soybeans with all three rain treatments, but that the depression was greatest with the most acidic rain. Ozone concentrations equal to or greater than those used in the studies are common in most areas of the Northeastern United States where acidic deposition is a problem (Jacobson et al., 1980b); therefore, the potential for possible ozone-acidic deposition interactions is great.

Shriner (1978a) studied the effect of acidic precipitation on host-parasite interactions. Simulated acid rain with a pH of 3.2 inhibited the development of bean rust and production of telia (a stage in the rust life cycle) by the oak-leaf rust fungus Cronartium fusiforme. It also inhibited reproduction of root-knot nematodes and inhibited or stimulated development of halo blight of bean seedlings depending on the time in the disease cycle during which the simulated acid rain was applied. The effects which inhibited disease development could result in a net benefit to plant health. Shriner (1976, 1980) also observed that root nodulation by Rhizobium on common beans and soybeans was inhibited by the simulated acid rain, suggesting a potential for reduced nitrogen fixation by legumes so affected.

Plants such as mosses and lichens are particularly sensitive to changes in precipitation chemistry because many of their nutrient requirements are obtained directly through precipitation. These plant forms are typically absent from regions with high chronic SO_2 air pollution and may be affected by acidic precipitation (Nieboer et al., 1976; Denison et al., 1977; Sheridan and Rosenstreter, 1973). Gorham (1976) and Giddings and Galloway (1976) have written reviews concerning this problem. Most investigations on the effects of air pollution on epiphytes have dealt with gaseous pollutants. Very few studies have considered acidic precipitation. Denison et al. (1977), however, did observe that the nitrogen-fixing ability of the epiphytic lichen Lobaria oregana was reduced when treated with simulated rainfall with a pH of 4.0 and below. Investigations concerning the effects of acidic precipitation on epiphytic microbial populations are very few (Abrahamsen and Dollard, 1979).

Limited fertilization could occur in the bracken fern Pteridium aquilinum under conditions of acidic precipitation (pH and sulfate concentrations) that prevail in the northeastern United States. Evans and Bozzone (1977), using buffered solutions to simulate acidic precipitation, observed that flagellar movement of sperm was reduced at pH levels below 5.8. Fertilization was reduced after exposure to pH's below 4.2. Sporophyte production was also reduced by 50 percent at pH levels below 4.2 when compared to 5.8. Addition of sulfate as sulfuric acid (86 mM) to the buffered solutions decreased fertilization at least 50 percent at all pH values observed. In another study, Evans and Bozzone (1978) observed that both sperm motility and fertilization in gametophytes of Pteridium aquilinum were reduced when anions of sulfate, nitrate, and chloride were added to buffered solutions.

Sulfur and nitrogen in precipitation have been shown to play an important role in vegetational response to acidic deposition. Jacobson et al. (1980b) investigated the impact of simulated acidic rain on the growth of lettuce at acidities of pH 5.7 and 3.2. At pH 3.2, solutions with $NO_3:SO_4$ mass ratios of 20:1, 2:1, and 1:7.5 were compared. For those growth parameters (root dry weight and apical leaf dry weight) that responded to the treatments, the results of the high nitrate concentrations applied at pH 3.2 could not be distinguished from the control treatment at pH 5.7. The effects, however, were significantly less than those obtained from the low nitrogen, high sulfur treatment. These observations suggest that sulfur was possibly a limiting factor in the nutrition of these plants, with the result that the plant response to sulfur overwhelmed the hydrogen ion effect. Other studies also have cited the beneficial effects of simulated acidic precipitation. Irving and Miller (1978) observed that an acidic simulant had a positive effect on productivity of field-grown soybeans as reflected by seed weight. Increased growth was attributed to a fertilizing effect from sulfur and nitrogen delaying senescence. Irving and Miller (1978), in the same study, also exposed soybeans to SO_2 and acidic precipitation. No visible injury was apparent in any of the plots; however, a histological study revealed significant increases in the number of dead mesophyll cells in all plots when compared to the control. The proportion of dead mesophyll cells of plants exposed to acid rain and SO_2 combined was more than additive when compared to the effects of each taken singly. Wood and Bormann (1977) reported an increase in needle length and the weight of seedlings of Eastern white pine with increasing acidity of simulated precipitation where sulfuric and nitric acid were used to acidify the mist. Increased growth was attributed to increased NO_3^- application. Abrahamson and Dollard (1979) also presented data suggesting positive growth responses in forest tree species resulting from nitrogen and sulfur in simulated rain. Simulated acidic precipitation was observed to increase the growth of Scots pine saplings in experiments conducted in Norway. Saplings in plots watered with acid rain of pH 3.0, 2.5, and 2.0 grew more than the control plots. The application of acid rain increased the nitrogen and sulfur content of the needles. As the acidity of the artificial rain was adjusted using sulfuric acid only, the increased growth was probably due to increased nitrogen mineralization and uptake. Turner and Lambert (1980) reported evidence indicating a positive growth response in Monterey pine from the deposition of sulfur in ambient precipitation in Australia.

Acidifying forest soils that are already acid by acidic precipitation or air pollutants is a slow process. Growth effects probably could not be detected for a long time. To identify the possible effects of acidification on poor pine forests, Tamm et al. (1977) conducted experiments using 50 kg and 100 kg of sulfur per hectare as dilute sulfuric acid (0.4 percent) applied annually with and without NPK (nitrogen, phosphorous, potassium) fertilizer. Nitrogen was found to be the limiting factor at both experimental sites. Acidification produced no observable influence on tree growth. Lysimeter and soil incubation experiments conducted at the same time as the experiments described above suggest that even moderate additions of sulfuric acid or sulfur to soil affect soil biological processes, particularly nitrogen turnover. The soil incubation studies indicated that additions of sulfuric acid increased the amount of mineral nitrogen but lowered the amount of nitrate.

Soil fertility may increase as a result of acidic precipitation as nitrate and sulfate ions, common components of chemical fertilizers, are deposited; however, the advantages of such additions are possibly short-lived as depletion of nutrient cations through accelerated leaching could eventually retard growth (Wood, 1975). Laboratory investigations by Overrein (1972) have demonstrated that leaching of potassium, magnesium, and calcium, all important plant nutrients, is accelerated by increased acidity of rain. Field studies in Sweden correlate decreases in soil pH with increased additions of acid (Oden et al., 1972).

Major uncertainty in estimating effects of acid rain on forest productivity is the capacity of forest soils to buffer against leaching by hydrogen ions. Forest canopies have been found to filter 90 percent of the hydrogen ions from rain (pH 4.0) falling on the landscape during the growing season (Eaton et al., 1973). As a result, solutions reaching the forest floor are less acidic (pH 5.0). Mayer and Ulrich (1977), however, point out that their studies suggest that for most elements the addition by precipitation (wetfall plus dryfall) to the soil beneath the tree canopy is considerably larger than that by precipitation to the canopy surface as measured by rain gauges on a non-forested area. The leaching of metabolites, mainly from leaf surfaces, and the washing out from leaves, branches, and stems of airborne particles and atmospheric aerosols intercepted by trees from the atmosphere, are suggested as the main reasons for the mineral increase.

Forest ecosystems are complicated biological organizations. Acidic precipitation will cause some components within the ecosystem to respond even though it is not possible at present to evaluate the changes that occur. The impact of the changes on the ecosystem can only be determined with certainty after the passage of a long period of time.

7.3.2.3 Effects on Human Health--One effect of acidification that is potentially of concern to human health is the possible contamination by toxic metals of edible fish and of water supplies. Studies in Sweden (Landner and Larsson, 1975; Turk and Peters, 1977), Canada (Tomlinson, 1979; Brouzes et al., 1977), and the United States (Tomlinson, 1979) have revealed high mercury concentrations in fish from acidified regions. Methylation of mercury to monomethyl mercury occurs at low pH while dimethyl mercury forms at higher pH (Fageström and Jernelöv, 1972). Monomethyl mercury in the water passing through the gills of fish reacts with thiol groups in the hemoglobin of the blood and is then transferred to the muscle. As methyl mercury is eliminated very slowly from fish, it accumulates with age.

Tomlinson (1979) reports that in the Bell River area of Canada precipitation is the source of mercury. Both methyl mercury and inorganic mercury were found in precipitation. The source of mercury in snow and rain was not known at the time of the study.

Zinc, manganese, and aluminum concentrations also increase as the acidity of lakes increases (Schofield, 1976b). The ingestion of fish contaminated by these metals is a distinct possibility.

Another human health aspect is the possibility that, as drinking-water reservoirs acidify owing to acidic precipitation, the increased concentrations of metals may exceed the public-health limits. The increased metal concentrations in drinking water are caused by increased watershed weathering and, possibly more importantly, increased leaching of metals from household plumbing. Indeed, in New York State, water from the Hinckley Reservoir has acidified to such an extent that "lead concentrations in water in contact with household plumbing systems exceed the maximum levels for human use recommended by the New York State Department of Health" (Turk and Peters, 1977). The lead and copper concentrations in pipes which have stood over night (U) and those in which the water was used (F) are depicted in Table 7-11.

TABLE 7-11. LEAD AND COPPER CONCENTRATION AND pH OF WATER FROM PIPES CARRYING OUTFLOW FROM HINCKLEY BASIN AND HANNS AND STEELE CREEK BASIN, NEAR AMSTERDAM, NEW YORK

Collection site and date	Pipe condition[1]	Copper (µg/l)	Lead (µg/l)	pH
Hinckley Dam				
Nov. 21, 1974	U	600	66	---
Nov. 21, 1974	F	20	2	7.4
Nov. 7, 1974	U	460	40	6.3
Nov.7, 1974	F	37	6	6.3
Oct. 1, 1974	U	570	52	6.8
Oct. 1, 1974	F	30	5	7.1
Aug. 15, 1974	U	760	88	6.3
Aug. 15, 1974	F	40	2	6.3
Amsterdam				
Jan. 6, 1975	U	2900	240	4.5
Jan. 6, 1975	F	80	3	5.0

[1] U, unflushed, (water stands in pipes all night); F, flushed.
Source: Turk and Peters (1979).

7.3.2.4 Effects of Acidic Precipitation on Materials--Acidic precipitation can damage the abiotic as well as the biotic components of an ecosystem. Of particular concern in this section are the deteriorative effects of acidic precipitation on materials and cultural artifacts of manmade ecosystems. At present, in most areas, the dominant factor in the formation of acidic precipitation is sulfur, usually as sulfur dioxide (Likens, 1976; Cowling and Dochinger, 1978). Because of this fact, it is difficult to isolate the effect of acidic precipitation from changes induced by sulfur pollution in general. (The effects of sulfur oxides on materials are discussed in Chapter 10.) High acidity promotes corrosion because the hydrogen ions act as a sink for the electrons liberated during the critical corrosion process (Nriagu, 1978). Precipitation as rain affects corrosion by forming a layer of moisture on the surface of the material and by adding hydrogen (H^+) and sulfate (SO_2^{2-}) ions as corrosion stimulators. Rain also washes out the sulfates deposited during dry deposition and thus serves a useful function by removing the sulfate and stopping corrosion (Kucera, 1976). Rain plays a critical role in the corrosive process because in areas where dry deposition predominates, the washing effect is greatest, while in areas where the dry and wet deposition processes are roughly equal, the corrosive effect is greater (Kucera, 1976). The corrosion effect, particularly of certain metals, in areas where the pH of precipitation is very low may be greatly enhanced by that precipitation (Kucera, 1976). In a Swedish study, the sulfur content of precipitation, expressed as meq/m^2 per year, was found to correlate closely with the corrosion rate of steel. The metals most likely to be corroded by precipitation with a low pH are those whose corrosion resistance may be ascribed to a protective layer of basic carbonates, sulfates, or oxides, such as those used on zinc or copper. The decrease in pH of rainwater to 4.0 or lower may accelerate the dissolution of the protective coatings (Kucera, 1976).

Materials reported to be affected by acidic precipitation, in addition to steel, are: copper materials, linseed oil, alkyd paints on wood, antirust paints on steel, limestone, sandstone, concrete, and both cement-lime and lime plaster (Cowling and Dochinger, 1978).

Stone is one of the oldest building materials used by man and has traditionally been considered one of the most durable because structures such as the pyramids, which have survived since antiquity, are made of stone. What is usually forgotten is that the structures built with stone that was not durable have long since disappeared (Sereda, 1977).

Atmospheric sulfur compounds (mainly sulfur dioxide, with subsidiary amounts of sulfur trioxide and ammonium sulfate) react with the carbonates in limestone and dolomites, calcareous sandstone and mortars to form calcium sulfate (gypsum). The results of these reactions are blistering, scaling, and loss of surface cohesion which, in turn, induces similar effects in neighboring materials not in themselves susceptible to direct attack (Sereda, 1977).

Sulfates have been implicated by Winkler (1966) as very important in the disintegration of stone. The surface flaking on the Egyptian granite obelisk (Cleopatra's Needle) in Central Park, New York is cited as an example. The deterioration occurred within two years of its erection in 1880.

A classic example of the effects of the changing chemical climate on the stability of stone is the deterioration of the Madonna at Herten Castle, near Recklinghausen, Westphalia in Germany. The sculpture of porous Baumberg sandstone was erected in 1702. Pictures taken of the Madonna in 1908 shows slight-to-moderate damage during the first 206 years. The features of the Madonna--eyes, nose, mouth and hair--are readily discernable. In pictures taken in 1969 after 267 years, no features are visible (Cowling and Dochinger, 1978).

It is not certain in what form sulfur is absorbed into stone, as a gas (SO_2) forming sulfurous and/or sulfuric acid or whether it is deposited in rain. Rain and hoarfrost both contain sulfur compounds. Schaffer (1932) compared the sulfate ion in both rain and hoarfrost at Headingley, Leeds, England in 1932 (Table 7-12) and showed that the content of hoarfrost was approximately 7 times greater than rain. Wet stone surfaces unquestionably increase the condensation or absorption of sulfates. Stonework kept dry and shielded from rain, condensing dew, or hoarfrost will be damaged less by SO_2 pollution than stone surfaces which are exposed (Sereda, 1977).

TABLE 7-12. COMPOSITION OF RAIN AND HOARFROST AT HEADINGLEY, LEEDS

	Average rain parts per million	Hoarfrost parts per million
Suspended matter	115	4620
Tar	15	158
Ash	28	67
Acidity	1.9	102.9
SO_3 as sulfur	22	148
SO_2 as sulfur	5.7	41.0
Total sulphur	27.7	189.0
Chlorine	7.3	94.6
Nitrogen as NH_3	1.98	8.57
Nitrogen as N_2O_5	0.196	0.0
Nitrogen as albuminoid	0.434	1.618

Source: Adapted from Schaffer (1932)

Acid rain may leach ions from stonework just as acidic runoff and ground water leaches ions from soils or bedrock; however, at the present time it is not possible to attribute the deleterious effects of atmospheric sulfur pollution to specific compounds.

Microbial action (an indirect result of sulfur deposition) can also contribute to the deterioration of stone surfaces. Tiano et al. (1975) isolated large numbers (250 to 20,000 cells per gram) of sulfate-reducing bacteria from the stones of two historical buildings of Florence, Italy. The majority of the bacteria belonged to the genus Thiobacillus. This genus of chemosynthetic aerobic microorganisms oxidize sulfide, elemental sulfur, and thiosulphate to sulfate to obtain energy (Andersson, 1978). Limestone buildings, and particularly the mortar used in the construction of brick and stone buildings, are susceptible to deterioration when conditions permit Thiobacillus to convert reduced forms of sulfur to sulfuric acid. Sulfate in acidic precipitation as well as other sulfur compounds deposited in dry deposition permit the formation of sulfur compounds utilizable by microorganisms. (For more information concerning the effects of sulfur oxides on materials, please consult Chapter 10.)

7.4 ASSESSMENT OF SENSITIVE AREAS

7.4.1 Aquatic Ecosystems

Why do some lakes become acidified by acidic precipitation and others not? What determines susceptibility? Are terrestrial ecosystems likely to be susceptible; if so, which ones?

The sensitivity of lakes to acidification is determined by: (1) the acidity of both wet deposition (precipitation) and dry deposition; (2) the hydrology of the lake; (3) the soil system, geology, and canopy effects; (4) the surface water. Given acidic precipitation, the soil system and associated canopy effects are most important. The hydrology of lakes includes the sources, amounts, and pathways of water entering and leaving a lake. The capability of a lake and its drainage basin to neutralize acidic contributions as well as the mineral content of its surface water is largely governed by the composition of the bedrock of the watershed. The chemical weathering of the watershed strongly influences the salinity (ionic composition) and the alkalinity of the surface water of a lake (Wetzel, 1975; Wright and Gjessing, 1976; Wright and Henriksen, 1978). The cation exchange capacity and weathering rate of the watershed and the alkalinity of the surface water determine the ability of the system to neutralize the acidity of precipitation.

Lakes vulnerable to acidic precipitation have been shown to have watersheds the geological compositions of which are highly resistant to chemical weathering (Wright and Gjessing, 1976; Galloway and Cowling, 1978; Wright and Henriksen, 1978). In addition, the watersheds of the vulnerable lakes usually have thin, poor soils and are poorly vegetated. The cation exchange capacity of such soils is low and, therefore, their buffering capacity is low (Schofield, 1979; Wright and Henriksen, 1978).

Wright and Henriksen (1978) point out that the chemistry of Norwegian lakes could be accounted for primarily on the basis of bedrock geology. They examined 155 lakes and observed that 59 of them lay in granite or felsic gneiss basins. Water in these lakes was low in most major ions and had low electrical conductivity. The fewer the minerals in water the lower its conductivity (Wetzel, 1975). The waters in the lakes surveyed were "among the softest waters in the world" (Wright and Henriksen, 1978). Sedimentary rocks generally weather readily, whereas igneous rocks are highly resistant. The Adirondacks, as pointed out by Schofield (1976a; 1979), have granite bedrock with much of the area covered with a mantle of mixed gneisses. Shallow soils predominate in the area. Thus, these areas are susceptible to acidification.

Limestone terrains, on the other hand, are capable of buffering intense concentrations of acids. Glacially derived sediment has been found to be more important than bedrock in assimilating acidic precipitation in the Canadian Shield area (Kramer, 1976). The detailed mineralology of the unconsolidated post-glacial cover is the most important parameter in assessing the H^+ ion assimilation of acid precipitation in non-calcareous terrain. Knowledge of the complete surface and subsurface hydrology is required as lower horizons may be calcareous, whereas surface deposits may be non-calcareous (Kramer 1976). Generally, however, bedrock geology is the best predictor of the sensitivity of aquatic ecosystems to acidic precipitation (Hendrey et al., 1980b).

Areas with aquatic ecosystems that have the potential for being sensitive to acidic precipitation are shown in Figure 7-27. In Figure 7-27, the shaded areas on the map indicate that the bedrock is composed of igneous or metamorphic rock while in the unshaded areas it is of calcareous or sedimentary rock. Metamorphic and igneous bedrock weathers slowly; therefore, lakes in areas with this type of bedrock would be expected to be dilute and of low alkalinity [<0.5 meq HCO_3^-/liter (Galloway and Cowling, 1978)]. Galloway and Cowling verified this hypothesis by compiling alkalinity data. The lakes having low alkalinity existed in regions having igneous and metamorphic rock (Galloway and Cowling, 1978). Hendrey et al. (1980b) have developed new bedrock geology maps of the eastern United States for predicting areas which might be impacted by acidic precipitation. The new maps permit much greater resolution for detecting sensitivity than has been previously available for the region.

Henriksen (1979) has developed a lake acidification "indicator model" using pH-calcium and calcium-alkalinity relationships as an indicator for determining increased surface water acidification. The indicator is based on the observation that in pristine lake environments (e.g., Northwest Norway or the Experimental Lakes area in northwest Ontario, Canada) calcium is accompanied by a proportional amount of bicarbonate because carbonic acid is the primary chemical weathering agent. The pH-calcium relationship found for such regions is thus defined as the reference level for unacidified lakes. Acidified lakes (e.g., Southeast Norway and the Adirondack region) will exhibit lower pH or lower alkalinity than the reference lakes, at comparable calcium levels, due to the replacement of bicarbonate by strong acid anions. (See Section 7.3.1.1).

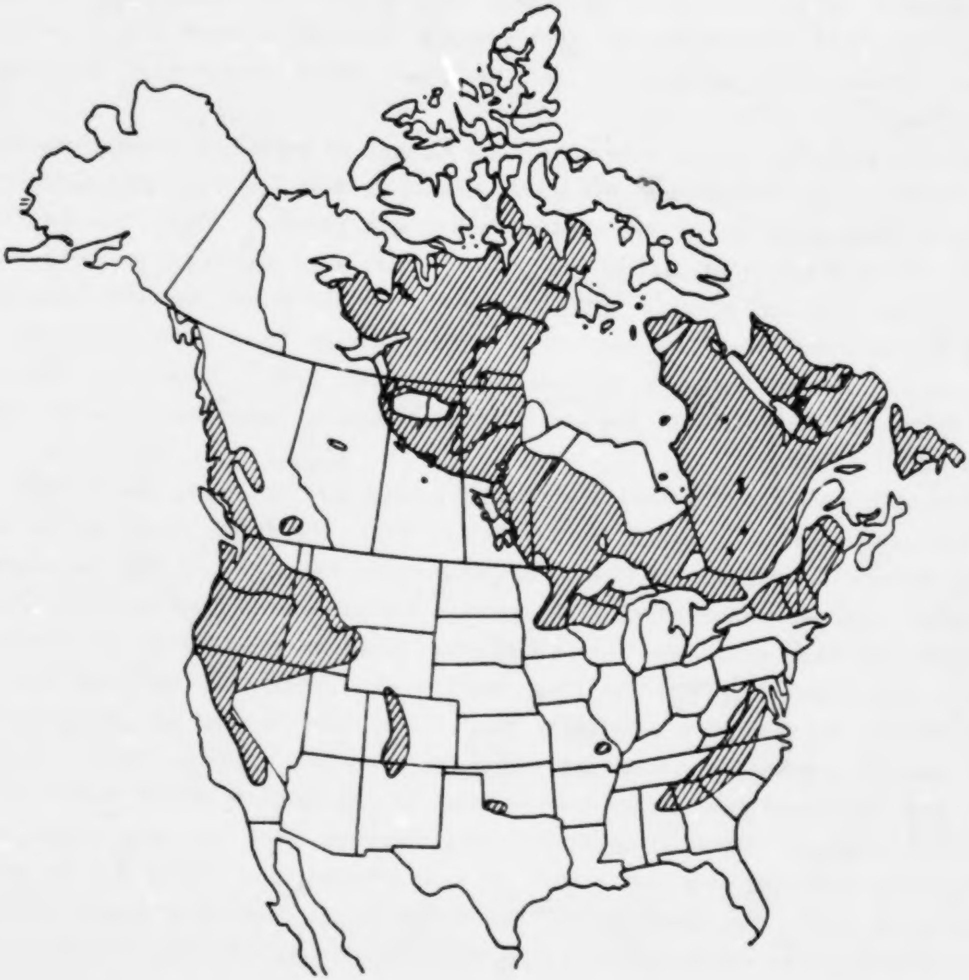


Figure 7-27. Regions in North America with lakes that are sensitive to acidification by acid precipitation by virtue of their underlying bedrock characteristics.

Source: Galloway and Cowling (1978).

A report by Hendrey et al. (1980b) compared pre-1970 data with post-1975 data. A marked decline in both alkalinity and pH was noted in waters of North Carolina and New Hampshire sensitive to acidification. In the former, pH and alkalinity have decreased in 80 percent of the streams tested and, in the latter, pH has decreased in 90 percent of the streams tested since 1949. These areas are predicted to be sensitive by geological mapping on the basis of their earlier alkalinity values. Detailed county by county maps of other states in the eastern United States suggest the sensitivity of these regions to acidic precipitation.

Though bedrock geology generally is a good predictor of the susceptibility of an area to acidification due to acidic precipitation, other factors also have an influence. Florida, for example, is underlaid by highly calcareous and phosphate rock, suggesting that acidification of lakes and streams is highly unlikely. Many of the soils, however, (particularly in northern Florida) are very mature and have been highly leached of calcium carbonate; as a result, some lakes in which groundwater inflow is minimal have become acidified (Hendrey and Brezonik, 1980). Conversely, there are areas in Maine with granitic bedrock where lakes have not become acidified, despite receiving precipitation with an average pH of approximately 4.3, because the drainage basins contain lime-bearing till and marine clay (Davis et al., 1978). Small amounts of limestone in a drainage basin exert a strong influence on water quality in terrain which would otherwise be vulnerable to acidification. Soils in Maine in the areas where the pH of lakes has decreased due to acidic precipitation are immature, coarse, and shallow, are derived largely from granitic material, and commonly have a low capacity for assimilating hydrogen ions from leachate and surface runoff in lake watersheds (Davis et al., 1978). The occurrence of limestone outcroppings in the Adirondack Mountains of New York State is highly correlated with lake pH levels. The occurrence of limestone apparently counteracts any effects of acidic precipitation. Consequently, when predicting vulnerability of a particular region to acidification, a careful classification of rock mixtures should be made. Rock formations should be classified according to their potential buffering capacity, and the type of soil overlying the formations should be noted. Local variations in bedrock and soils are very important in explaining variations in acidification among lakes within an area.

7.4.2 Terrestrial Ecosystems

Predicting the sensitivity of terrestrial ecosystems to acidic precipitation is much more difficult than for aquatic ecosystems. With aquatic ecosystems, it is possible to compare affected and unaffected ecosystems and to note where the changes have occurred. With terrestrial ecosystems, comparisons are difficult to make because the effects of acidic precipitation have been difficult to detect. Therefore, predictions regarding the sensitivity of terrestrial ecosystems must, as much as possible, use the data which link the two ecosystems, i.e., data on bedrock geology. Since, in most regions of the world, bedrock is not exposed but is covered with soil, it is the sensitivity of different types of soil which must be assessed. Therefore, the first step is to define "sensitivity" as it is used here in relation to soils and acidic precipitation. Sensitivity of soils to acidification alone, though it may be the most important long-term effect, is too narrow a concept. Soils influence the quality of waters in associated streams and lakes and may be changed in ways other than simple pH-base saturation relationships, e.g., microbiological populations of the surface layers or accelerated loss of aluminum by leaching. Therefore, criteria need to be used that would relate soil "sensitivity" to any important change brought about in the local ecosystem by acidic precipitation (McFee, 1980).

All soils are not equally susceptible to acidification. Sensitivity to leaching and to loss of buffering capacity varies according to the type of parent material from which a soil is derived. Buffering capacity is greatest in soils derived from sedimentary rocks, especially those containing carbonates, and least in soils derived from hard crystalline rocks such as granites and quartzites (Gorham, 1958). Soil buffering capacity varies widely in different regions of the country. Unfortunately, many of the areas now receiving the most acidic precipitation are also those with relatively low natural buffering capacities.

The buffering capacity of soil depends on mineralogy, texture, structure, organic matter, pH, base saturation, salt content, and soil permeability. Above a pH of 5.5 virtually all of the H^+ ions, irrespective of source, are retained by ion exchange and chemical weathering. Below pH 5.5, the retention of the H^+ ion decreases with the soil pH in a manner determined by the composition of the soil (Donahue et al., 1977). With a successive drop in the soil pH below 5.0, an increasing proportion of hydrogen ions (H^+) and deposited sulfuric acid will pass through the soil and acidify runoff water (Donahue et al., 1977). The sensitivity of different soils based on pH, texture, and calcite content is summarized in Table 7-13.

Soils are the most stable component of a terrestrial ecosystem. Any changes which occur in this component would probably have far-reaching effects. McFee (1980) has listed four

TABLE 7-13. THE SENSITIVITY TO ACID PRECIPITATION BASED ON: BUFFERING CAPACITY AGAINST pH-CHANGE, RETENTION OF H^+, AND ADVERSE EFFECTS ON SOILS

	Calcareous soils	Noncalcareous clays pH > 6	Noncalcareous sandy soils pH > 6	Cultivated soils pH > 5	Acid soils pH < 5
Buffering	Very high	High	Low	High	Moderate
H^+ retention	Maximal	Great	Great	Great	Slight
Adverse effects	None	Moderate	Considerable	None - slight	Slight

Source: Wiklander (1979).

parameters which are of importance in estimating the sensitivity of soils to acidic precipitation. They are:

1. the total buffering or cation exchange capacity, which is provided primarily by clay and soil organic matter.
2. the base saturation of that exchange capacity, which can be estimated from the pH of the soil.
3. the management system imposed on the soil; is it cultivated and amended with fertilizers or lime or renewed by flooding or by other additions?
4. the presence or absence of carbonates in the soil profile.

McFee (1980) mapped soils of the Eastern United States taking into account several factors, e.g., the sensitivity to acidic precipitation, effects of cultivation (Figure 7-28). The areas containing most of the soils potentially sensitive to acidic precipitation are in the upper Coastal Plain and Piedmont regions of the southeast, along the Appalachian Highlands, through the east central and northeastern areas, and in the Adirondack Mountains of New York (McFee, 1980). The current limited state of knowledge regarding the effects of acidic precipitation on soils makes a more definitive judgment of the location of areas with the most sensitive soils difficult at the present time.

The capacity of soils to absorb and retain anions, also important in determining whether soils will become acidified, was not discussed by McFee (1980). The capacity for anion absorption is great in soils rich in hydrated oxides of aluminum (Al) and iron (Fe). Reduced leaching of salt cations is of great significance not only in helping to prevent soil acidification but in geochemical circulation of nutrients, fertilization in agriculture and preventing water pollution (Wiklander, 1980; Johnson et al. 1980; Johnson, 1980). (See Section 7.3.2.1.) This parameter, as well as those listed by Mc Fee (1980), should be used in determining the sensitivity of soils to acidification by both wet and dry deposition.

7.5 SUMMARY

Occurrence of acidic precipitation (rain and snow) in many regions of the United States, Canada, and Scandanavia has been implicated in the disappearance or reduction of fish, other animals, and plant life in ponds, lakes, and streams. In addition, acidic precipitation appears to possess the potential for impoverishing sensitive soils, degrading natural areas, injuring forests, and damaging stone monuments and buildings.

Sulfur and nitrogen oxides, emitted through the combustion of fossil fuels, have been implicated as the chief contributors to the acidification of precipitation. The fate of sulfur and nitrogen oxides, as well as other pollutants emitted into the atmosphere, depends on their dispersion, transport, transformation, and deposition. Emissions from automobiles occur at ground level, those from electric power generators from smoke stacks 300 meters (1000 feet) or more in height. Transport and transformation of the sulfur and nitrogen oxides are in part associated with the height at which they are emitted. The greater the height, the greater the likelihood of a longer residence time in the atmosphere and a greater opportunity for the

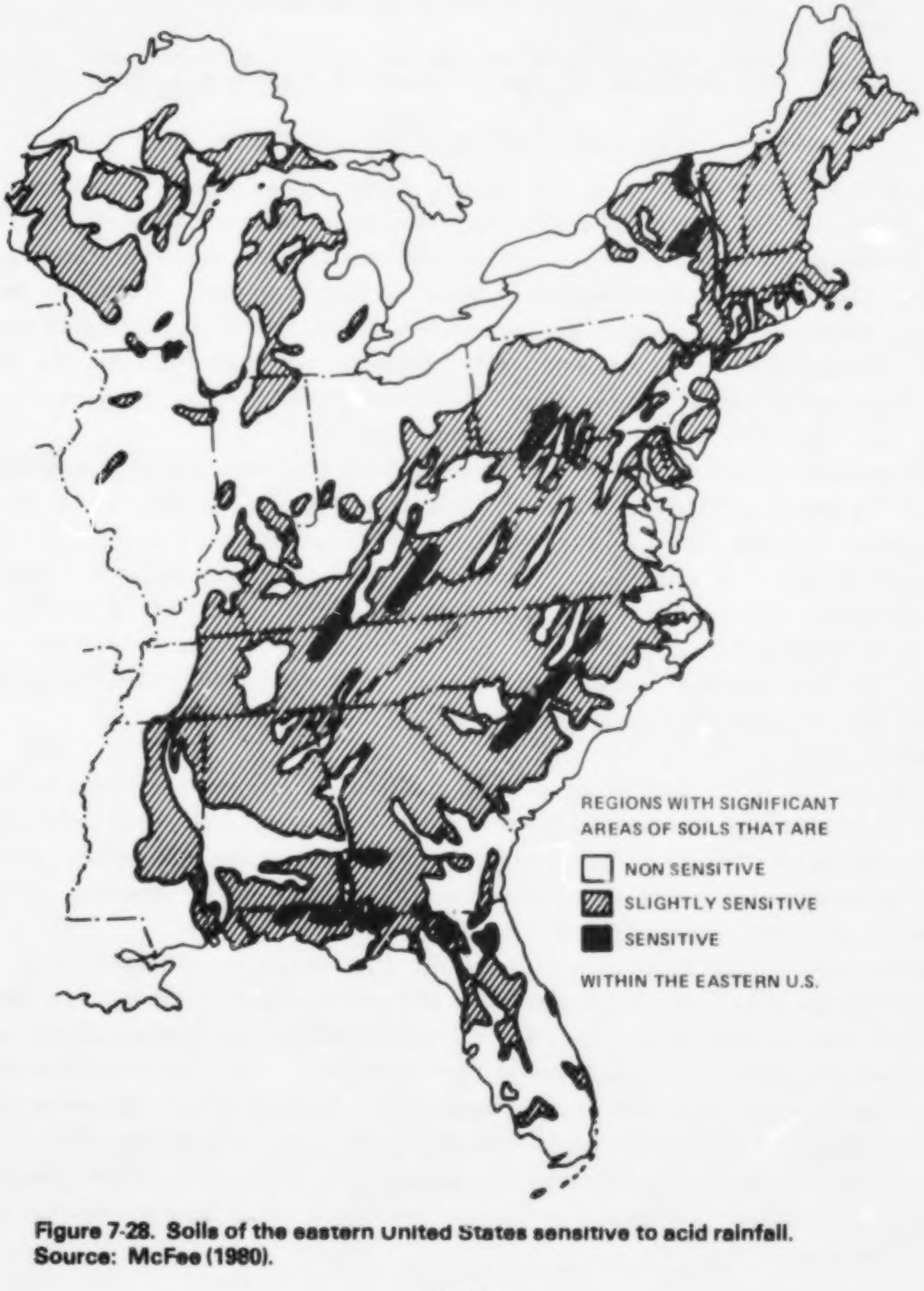

REGIONS WITH SIGNIFICANT AREAS OF SOILS THAT ARE
☐ NON SENSITIVE
▨ SLIGHTLY SENSITIVE
■ SENSITIVE
WITHIN THE EASTERN U.S.

Figure 7-28. Soils of the eastern United States sensitive to acid rainfall. Source: McFee (1980).

chemical transformation of the oxides to sulfates, nitrates or other compounds. Ozone and other photochemical oxidants are believed to be involved in the chemical transformations. Because of long range transport, acidic precipitation in a particular state or region can be the result of emissions from sources in states or regions hundreds of miles away rather than local sources. To date the complex nature of the chemical transformation processes has not made possible the demonstration of a direct cause-and-effect relationship between emissions of sulfur and nitrogen oxides and the acidity of precipitation.

Natural emissions of sulfur and nitrogen compounds are also involved in the formation of acidic precipitation; however, in industrialized regions anthropogenic emissions exceed natural emissions.

Precipitation is arbitrarily defined as being acidic if its pH is less than 5.6. Currently the acidity of precipitation in the Northeastern United States, the region most severely impacted, ranges from pH 3.0 to 5.0. Precipitation episodes with a pH as low as 3.0 have been reported for other regions of the United States. The pH of precipitation can vary from event to event, from season to season and from geographical area to geographical area.

The impact of acidic precipitation on aquatic and terristrial ecosystems is not the result of a single or several precipitation events, but the result of continued additions of acids or acidifying substances over time. Wet deposition of acidic substances on freshwater lakes, streams, and natural land areas is only part of the problem. Acidic substances exist in gases and particulate matter transferred into the lakes, streams, and land areas by dry deposition. Therefore all the observed biological effects should not be attributed to acidic precipitation alone.

Sensitivity of a lake to acidification depends on the acidity of both wet and dry deposition, the soil system of the drainage basin, canopy effects of ground cover and the composition of the watershed bedrock.

An extremely close mutual relationship exists between the chemistries of the environment and of living organisms. There is a continuing exchange of nutrients and of energy. The two are closely intertwined responses. There is no action without a reaction. Ecosystems can respond to environmental changes or perturbations only through the response of the populations of organisms of which they are composed. Species of organisms sensitive to specific environmental changes are removed. Therefore, the capacity of an ecosystem to maintain internal stability is determined by the ability of individual organisms to adjust their physiology or behavior to environmental change. The success with which an organism copes with environmental changes is determined by its ability to yield reproducing offspring. The size and success of a population depends upon the collective ability of organisms to reproduce and maintain their numbers in a particular environment. Those organisms that adjust best contribute most to future generations because they have the greatest number of progeny in the population.

The capacity of organisms to withstand injury from weather extremes, pesticides, acidic deposition, or polluted air follows the principle of limiting factors. According to this principle, for each physical factor in the environment there exists for each organism a minimum and maximum limit beyond which no members of a particular species can survive. Either too much or too little of a factor such as heat, light, water, or minerals (even though they are necessary for life) can jeopardize the survival of an individual and in extreme cases a species. When one limiting factor is removed another takes its place. The range of tolerance of an organism may be broad for one factor, narrow for another. The tolerance limit for each species is determined by its genetic makeup and varies from species to species for the same reason. The range of tolerance also varies depending on the age, stage of growth or growth form of an organism. Limiting factors are, therefore, factors which, when scarce or overabundant, limit the growth, reproduction and/or distribution of an organism. The increasing acidity of water in lakes and streams appears to be such a factor. Significant changes that have occurred in aquatic ecosystems with increasing acidity include the following:

1. Fish populations are reduced or eliminated.
2. Bacterial decomposition is reduced and fungi may dominate saprotrophic communities. Organic debris accumulates rapidly, tying up nutrients, and limiting nutrient mineralization and cycling.
3. Species diversity and total numbers of species of aquatic plants and animals are reduced. Acid-tolerant species dominate.
4. Phytoplankton productivity may be reduced due to changes in nutrient cycling and nutrient limitations.
5. Biomass and total productivity of benthic macrophytes and algae may increase due partially to increased lake transparency.
6. Numbers and biomass of herbivorous invertebrates decline. Tolerant invertebrate species, e.g., air-breathing bugs (water-boatmen, back-swimmers, water striders) may become abundant primarily due to reduced fish predation.
7. Changes in community structure occur at all trophic levels.

Studies indicate that pH levels between 6.0 and 5.0 inhibit reproduction of many species of aquatic organisms. Fish populations become seriously affected at a pH lower than 5.0.

Disappearance of fish from lakes and streams follows two general patterns. One results from sudden short-term shifts in pH, the other arises from a long-term decrease in the pH of the water. A major injection of acids and other soluble substances occurs when polluted snow melts during warm periods in winter or early spring. Fish kills are a dramatic consequence of such episodic injections.

Long-term increases in acidity interfere with reproduction and spawning, producing a decrease in population density and a shift in size and age of the population to one consisting primarily of larger and older fish. Effects on yield often are not recognizable until the population is close to extinction; this is particularly true for late-maturing species with long lives. Even relatively small increases (5 to 50 percent) in mortality of fish eggs and fry can decrease yield and bring about extinction.

Aluminum is mobilized at low pH values. Aluminum may be as important or more important than pH levels as factors leading to declining fish populations in acidified lakes. Certain aluminum compounds in the water upset the osmoregulatory function of the blood in fish. Aluminum toxicity to aquatic biota other than fish has not been assessed.

An indirect effect of acidification potentially of concern to human health is possible heavy metal contamination of edible fish and water supplies. Studies in Canada and Sweden reveal high mercury concentrations in fish from acidified regions. Lead and copper have been found in plumbing systems with acidified water, and persons drinking the water could suffer from lead poisoning.

Acidic precipitation may indirectly influence terrestrial plant productivity by altering the supply and availability of soil nutrients. Acidification increases leaching of plant nutrients (such as calcium, magnesium, potassium, iron, and manganese), increases the rate of weathering of most minerals, and also makes phosphorus less available to plants. Acidification also decreases the rate of many soil microbiological processes such as nitrogen fixation by Rhizobium bacteria on legumes and by the free-living Azotobacter, mineralization of nitrogen from forest litter, nitrification of ammonium compounds, and overall decay rates of forest floor litter.

Plants usually take up sulfur in the form of sulfate from the soil; however, they can also take up SO_2 from the atmosphere through their leaves and utilize it as a sulfur source for plant nutrition. If soil sulfur is low, plants may obtain most of their required sulfur from the atmosphere. Though small amounts of SO_2 may be beneficial, large amounts and high frequency of uncontrolled applications can be detrimental in the long term.

At present, there are no documented observations or measurements of changes in natural terrestrial ecosystems that can be directly attributed to acidic precipitation. This does not necessarily indicate that none are occurring. The information available on vegetational effects is an accumulation of the results of a wide variety of controlled research approaches largely in the laboratory, using in most instances some form of "simulated" acidic rain, frequently dilute sulfuric acid and/or nitric acid. The simulated "acid rains" have deposited hydrogen (H^+), sulfate ($SO_4^=$) and nitrate (NO_3^-) ions on vegetation and have caused necrotic lesions in a wide variety of plants species under greenhouse and laboratory conditions. Such results must be interpreted with caution, however, because the growth and morphology of leaves under greenhouse conditions are often atypical of field conditions. Based on laboratory studies, sensitivity of plants to acidic depositions seems to be associated with the wettability of leaf surfaces. The shorter the time of contact, the lower the resulting dose, and the less likelihood of injury.

Erosion of stone monuments and buildings and corrosion of metals can result from acidic precipitation. Because sulfur compounds are a dominant component of acidic precipitation and are deposited during dry deposition also, the effects resulting from the two processes cannot be distinguished. In addition, the deposition of sulfur compounds on stone surfaces provides a medium for microbial growth that can result in deterioration.

Certain aspects of the acidic deposition issue remain subject to debate because existing data are ambiguous or inadequate. A comprehensive evaluation of scientific evidence bearing on these issues is being prepared as part of a forthcoming EPA critical assessment document on acidic deposition.

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